



## DEVELOPMENT OF POLYPHENYLQUINOXALINE GRAPHITE COMPOSITES

By

J. T. HOGGATT

S. G. HILL

J. G. SHDO

The Boeing Aerospace Company  
Seattle, Washington 98124

July, 1974

Prepared for  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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NASA LEWIS RESEARCH CENTER  
CONTRACT NAS 3-16799

P. DELVIGS, PROJECT MANAGER

(NASA-CR-134674) DEVELOPMENT OF  
POLYPHENYLQUINOXALINE GRAPHITE COMPOSITES  
Final Report, 1 Apr. 1973 - 15 Jun.  
1974 (Boeing Aerospace Co., Seattle,  
Wash.)  
CSC 11D G3/18 47774  
N74-32018  
Unclas

1. Report No. NASA CR- 134674		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle DEVELOPMENT OF POLYPHENYLQUINOXALINE GRAPHITE COMPOSITES				5. Report Date July, 1974	
				6. Performing Organization Code ASG 2-5540	
7. Author(s) J.T. HOGGATT, S.G. HILL, J.G. SHDO				8. Performing Organization Report No.	
9. Performing Organization Name and Address THE BOEING AEROSPACE COMPANY P.O. Box 3999 Seattle, Wash. 98124				10. Work Unit No.	
				11. Contract or Grant No. NAS 3-16799	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				13. Type of Report and Period Covered CONTRACTOR REPORT - FINAL April 1, 1973 ~ June 15, 1974	
				14. Sponsoring Agency Code	
15. Supplementary Notes PROJECT MANAGER, Dr. P. Delvigs Materials and Structure Division NASA-Lewis Research Center Cleveland, Ohio 44135					
16. Abstract <p>This exploratory program was divided into four basic tasks. The initial phase was devoted toward investigating processing variables associated with previously developed PPQ resins. These polymers were derived from p-bis(phenylglyoxalyl)benzene reacted with 3,3'-diaminobenzidine and/or 3,3',4,4'-tetraminobenzophenone. Four new phenylquinoxaline polymers were synthesized and characterized in Tasks II and III. These consisted of a hydroxyl group containing PPQ synthesized from 3,3'-diaminobenzidine (DAB), m-bis(phenylglyoxalyl)benzene and m-bis(p-hydroxyphenylglyoxalyl)benzene; a cyano group containing PPQ from the reaction of DAB and p-bis(p-cyanophenoxyphenylglyoxalyl)benzene; an end-capped block copolymer; and a polymer from the reaction of 3,3',4,4'-tetraminobenzophenone and m-bis(phenylglyoxalyl)benzene designated TAB/mBPGB. The latter two polymers were chosen for composite studies in the latter two tasks of the program.</p> <p>Mechanical properties of the graphite reinforced PPQ composites were determined over the temperature range of +21°C to 316°C. Flexural strengths of the HMS graphite fiber composites were in excess of <math>8.97 \times 10^8 \text{ N/m}^2</math> (130,000 psi) at +21°C (70°F) with over 50% strength retention at +316°C.</p>					
17. Key Words (Suggested by Author(s)) Polyphenylquinoxaline Graphite Reinforcement Heat-Resistant Composites Polymer Synthesis High-modulus Composites			18. Distribution Statement  UNCLASSIFIED - Distribution Unlimited		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified			

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## FOREWORD

This report presents the work accomplished by the Boeing Aerospace Company on NASA Contract NAS3-16799 "Development of Polyphenylquinoxaline Graphite Composites" during the period of April 1, 1973 to June 15, 1974. The program was sponsored by the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, 44135. The program was administered by the Materials and Structures Division, Polymers Section; Dr. Tito Serafini, Group Supervisor. Dr. P. Delvigs was Project Manager.

Performance of this contract was under the direction of the Materials Development Group, Research and Engineering Division of The Boeing Aerospace Company; Seattle, Washington. Mr. G. E. Hughes was Program Supervisor. Mr. J. T. Hoggatt was Program Manager and Technical Leader.

Mr. S. G. Hill was responsible for composite fabrication and evaluation. Monomers and polymers syntheses and characterization work was conducted by Mr. P. M. Hergenrother (Task I, II and III) and by Dr. J. G. Shdo (Task IV).

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In a previous NASA contract (NAS3-15547, Reference 1) the potential of polyphenylquinoxaline graphite reinforced composites to serve as heat resistant structural materials was demonstrated. However, from that program, several deficiencies in the polymers were noted that required additional investigation and also new avenues of investigation became apparent. One polymer that was developed and showed good performance was a block copolymer (1:3) PPQ derivative. Additional studies to optimize the processing parameters and to gain a better understanding of the parameters that influenced this polymer's heat resistance were warranted. It was also apparent that a higher degree of polymer cross-linking was needed in the phenylquinoxaline polymers, in general to gain thermal stability. Methods of obtaining this cross-linking appeared feasible.

This exploratory program was divided into four basic tasks. The initial phase was devoted toward investigating processing variables associated with previously developed PPQ resins (Reference 1). Tasks II and III involved new polymer synthesis and the characterization of the graphite reinforced composites resulting from them. The best polymers and composites from Task I-III were subjected to mechanical property characterization in Task IV. All the composite work was performed with high modulus (type HM-S) graphite fiber.

In Task I, processing parameters associated with composite fabrication from selected PPQ polymers were studied. These polymers were derived from p-bis(phenylglyoxalyl)benzene reacted with 3,3'-diaminobenzidine and/or 3,3',4,4'-tetraaminobenzophenone. These studies and studies reported in reference 2 indicated that a monomeric reactant (PMR) approach towards fiber impregnation was an attractive method of prepreg preparation when high viscosity polymers (e.g. PPQ's) are involved. Additional studies in Task I included effects of resin content and cure cycle on mechanical properties.

Four new phenylquinoxaline polymers were synthesized in Task II. These consisted of a hydroxyl group containing PPQ synthesized from 3,3'-diaminobenzidine (DAB), m-bis(phenylglyoxalyl)benzene and m-bis(p'-hydroxyphenylglyoxalyl)benzene; a cyano group containing PPQ from the reaction of DAB and p-bis(p'-cyanophenoxyphenylglyoxalyl)benzene; an end-capped block copolymer (Reference 1); and a polymer from the reaction of 3,3', 4,4'-tetraaminobenzophenone and m-bis(phenylglyoxalyl)benzene designated TAB/m-BPGB. The latter two polymers were chosen for composite studies in the latter two tasks of the program.

Mechanical properties of the graphite reinforced PPQ composites were good over the +21°C to 316°C temperature range. Flexural strengths of the HM-S graphite fiber composites were in excess of  $8.97 \times 10^8 \text{ N/m}^2$  (130,000 psi) at +21°C (70°F) with over 50% strength retention at +316°C. The polyphenylquinoxalines appear satisfactory for high temperature applications, however, studies to promote better polymer crosslinking and less stringent cure conditions (i.e., lower temperatures) are warranted.

Under NASA Contract NAS 3-15547 (Reference 1) a series of polyphenylquin-oxalines were evaluated. From that investigation, two polymers were chosen for more exploratory developments. These were (1) a copolymer made from the reaction of p-bis(phenylglyoxalyl)benzene, 3,3'-diaminobenzidine and 3,3',4,4'-tetraaminobenzophenone per Eq. 1 and (2) PPQ-I from the reaction of 3,3'-diaminobenzidine and p-bis(phenylglyoxalyl)benzene, Eq. 2. Studies in this task concentrated on the investigation of impregnation techniques, cure parameters and the effects of fiber volume on composite properties. Each of these areas of investigation are discussed below. In the course of the investigations, PPQ-I was deleted and substituted with a polymer designated PPQ-II (Reference 1). PPQ-I was dropped due to poor fiber wetting. PPQ-II is a polymer derived from the reaction of p-bis(phenylglyoxalyl)benzene and 3,3',4,4'-tetraaminobenzophenone, Eq. 3.

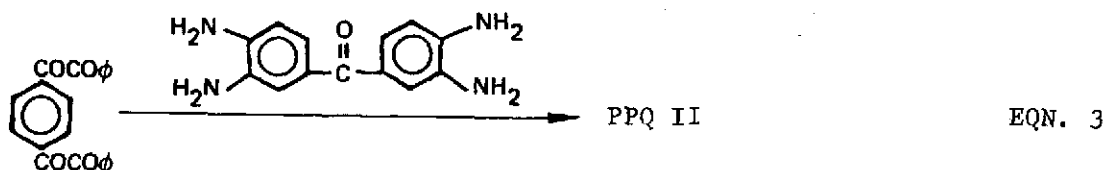
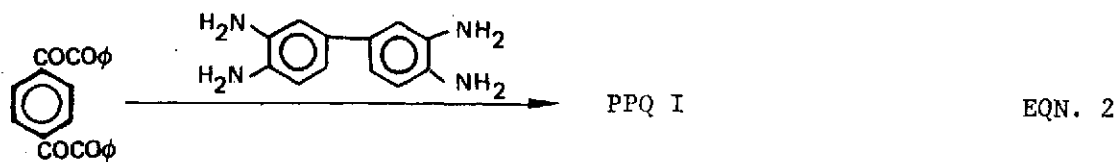
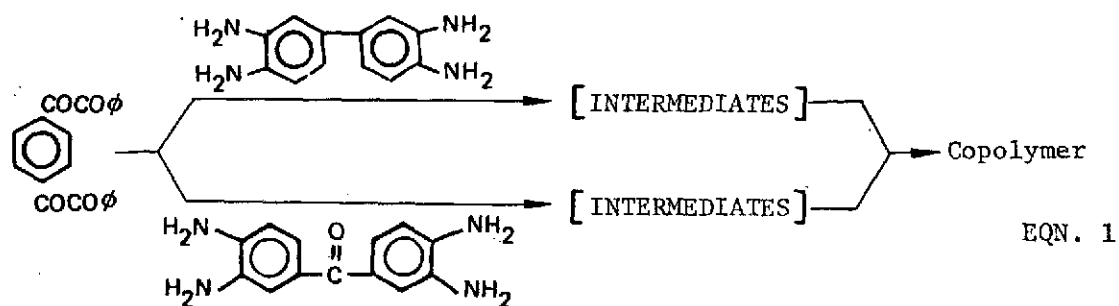


Table : 1 Characterization of Polymers

Item No.	Exp't No. PH-1-	Polymer	Stoichiometry <sup>1</sup> NH <sub>2</sub> /CO	R <sub>x</sub> Scale, Mole	Conc., % Solids <sup>2</sup>	Solvent	Sol'n Vis., cps <sup>3</sup>	$\eta$ inh, dl/g <sup>4</sup>	Tg, °C <sup>5</sup> (Tg after 0.5 h at 350° C)	PST, °C <sup>6</sup>
1	244	RaCo (1:3) via PMR	1.00/1.00	0.20	18	DMF	---	0.35	287 (333)	290-300
2	246	B1Co (1:3)	0.985/1.00	1.20	16.2	m-cresol xylene (1:1)	6250	1.06	324	317-325
3	247	TAB/ m-BPGB <sup>7</sup>	0.995/1.00	0.30	18	m-cresol xylene (1:1)	2250	0.85	285	295-305
4	254	PPQ-I via PMR	1.00/1.00	0.10	17.8	NMP	---	0.66 <sup>8</sup> 1.32 <sup>9</sup>	300 <sup>8</sup> (342) <sup>9</sup>	222-230 315-325
5	257	B1Co (1:3) End-capped	Polymer No. 2	---	---	---	---	1.07	325	318-327
6	267	PPQ II via PMR	1.00/1.00	0.30	18	DMF	---	0.13 <sup>10</sup> 0.4 <sup>11</sup>	245 <sup>10</sup> 312 <sup>11</sup>	230-237 312
7	269	Hydroxy/3PPQ <sup>7</sup>	1.00/1.00	.01	18	m-cresol	17,600	0.77	339 <sup>12</sup>	> 345
8	277	DAB/ p-CPGB <sup>7</sup>	1.00/1.00	.005	15	m-cresol	<sup>13</sup>	<sup>14</sup>	285 (287)	315-320
9	277-1	DAB/ p-CPGB	1.00/1.00	.005	10	m-cresol	---	<sup>14</sup>	---	---

<sup>1</sup> Mole ratio of tetraamine to tetracarbonyl monomer.

2. Based upon the weight of polymer and volume of solvent.

3. Brookfield viscosity at 25°C.

4. Inherent viscosity in 0.5% m-cresol solution at 25° C.

5. Glass transition temperature, determined by DSC ( $\Delta T = 20^\circ \text{C/min}$  in N<sub>2</sub>).

6. Polymer softening temperature, determined on Fisher-Johns melting point apparatus under slight pressure.

7. Hydroxy/3PPQ = 3,3'-diaminobenzidine (DAB), m-bis (p'-hydroxyphenylglyoxalyl) benzene (m-HPGB), and

m-bis (phenylglyoxalyl) benzene (m-BPGB). Para-bis (p'-cyanophenoxyphenylglyoxalyl) benzene = p-CPGB

8. After 10 minutes reaction time.

9. After 5 hours reaction time.

10. After 1 hour reaction time.

11. After 5 hours reaction time.

12. No Tg observed in the DSC after the polymer was exposed to 360°F.

13. Polymer solution was near gel and too viscous for Brookfield viscosity determinations.

14. Inherent viscosity was not determined because polymer could not be completely redissolved in m-cresol.



## 2.1 Impregnation Studies

This investigation was conducted to compare the effectiveness of impregnation using a diluted polymer solution vs. using a polymerization of monomeric reactants (PMR) approach. PPQ solutions are relatively viscous, and even at the 15-20% solid level care must be taken to insure good wetting of the graphite fiber bundle. The PMR approach, which was developed at NASA-Lewis (Reference 2), permits the fiber to be wetted with a low viscosity solution of monomeric reactants with the polymer formation and the accompanying increase in viscosity occurring on the fiber. The standard method of fiber impregnation is described in detail in Section 8.0, Appendix. The PMR approach was tried using three different polymers. These were a random copolymer (1:3), PPQ-I and PPQ-II (Reference 1). The systems were impregnated and dried using the same procedures as with the standard method except the impregnating resins were solutions of monomeric reactants rather than polymer. The detailed preparation procedure for each reactant is given in Section 8.0, Appendix. A summary of synthesis and characterization data of the polymers which were used in this task, and in later tasks, are shown in Table 1. The method of preparation for each monomeric reactant solution follows.

### 2.1.1 Random Copolymer

A random copolymer (Item No. 1, Table 1) was prepared from reaction of 3,3'-diaminobenzidine (0.05 mole) and 3,3',4,4'-tetraaminobenzophenone (0.15 mole) with p-bis(phenylglyoxalyl)benzene (0.20 mole) in dimethylformamide at 18% solids content. After stirring ~0.5 hour, the major portion of the dark red solution was used to impregnate the HM-S graphite fibers. The remaining solution was stirred 20 hours with the appearance of turbidity. The polymer was precipitated and washed with methanol, dried and characterized as shown in Table 1. The inherent viscosity of the polymer was low (0.35 dl/g) which explains the initial low glass transition temperature ( $T_g = 287^\circ\text{C}$ ) of the polymer. However, the  $T_g$  increased to  $333^\circ\text{C}$  after holding in the DSC apparatus for 0.5 hour at

### 2.1.1 (Continued)

350°C. This increase was presumably due to further chain growth. The Tg of high molecular weight random phenylquinoxaline copolymer (1:3) was 325°C (Reference 1).

A second laminate was made with the random copolymer solution to determine the influences of impregnation methods on laminate properties. The prepreg for the second laminate was made by vacuum impregnation of a flat sheet rather than drum winding.

The vacuum impregnated material was made by laying unidirectional fiber tows (8 tows per inch) between two layers of porous teflon-coated glass fabric and saturating the fibers with the PMR solution. The system was covered with FEP (teflon) film, sealed and placed under vacuum. The solution was worked into the fibers with the excess resin being removed at the edges. After remaining under vacuum for 16 hours under heat lamps at ~71°C (~160°F), the prepreg was further dried in an oven at 121°C (250°F) for 24 hours.

### 2.1.2 PPQ-I

PPQ-I, via the PMR route, (polymer No. 4, Table 1), was prepared from the reaction of stoichiometric quantities of 3,3'-diaminobenzidine and p-bis(phenylglyoxalyl)benzene in N-methylpyrrolidone (NMP) at 17.8% solids content. After stirring at ambient temperature for 10 minutes, a small portion of the blood red solution was isolated and quenched in methanol for inherent viscosity measurements. The isolated yellow polymer exhibited an  $\eta_{inh}$  of 0.66 and a Tg of 300°C. (The polymer may have undergone further chain growth while dissolved overnight in m-cresol to obtain the  $\eta_{inh}$  measurement). The remaining portion of the

## 2.1.2

## (Continued)

polymer solution was stirred an additional 0.5 hour and used to impregnate the drum wound graphite fibers. (Refer to paragraph 8.1.4). The polymer precipitated on the fibers almost immediately with total precipitation occurring within one hour. As result the polymer did not thoroughly wet the fibers. The short operating time was expected but a better degree of wetting was anticipated. An isolated sample of the same polymer batch required 5 hours to precipitate the polymer. This latter sample was stirred at ambient temperature and after 4.75 hours the solution viscosity had increased appreciably with polymer precipitation beginning after five hours. The polymer was isolated by quenching in methanol, washed well, dried, and characterized as shown in Table 1. The  $\eta_{inh}$  was 1.32 and the Tg after 0.5 hour at 350°C was 342°C. The Tg of PPQ-I ( $\eta_{inh} = 1.24$  as 0.5%  $H_2SO_4$  solution at 25°C) prepared during the previous contract was 350°C (Reference 1).

## 2.1.3

## PPQ-II

Because of the short working life of the PPQ-I (PMR) solution and the poor wetting characteristics, PPQ-II (Reference 1) was introduced to the program using the PMR technique. PPQ-II (Item 6, Table 1) was prepared at 18% solids in DMF from the reaction of 3,3',4,4'-tetraamino-benzophenone (0.30 mole) and p-bis(phenylglyoxalyl) benzene (0.30 mole). After stirring the blood red solution at ambient temperature for 1 hour, it was used for fiber impregnation. A small sample of the polymer was retained and isolated by quenching in methanol. The isolated polymer exhibited an  $\eta_{inh}$  of 0.13 dl/g (0.5% m-cresol solution at 25°C), a Tg of 245°C, and a polymer softening temperature (PST) of 230 to 237°C. Another sample of the polymer was stirred continuously to determine the amount of time required for polymer precipitation. After 5 hours of stirring, turbidity developed in the solution and after overnight stirring the polymer precipitated. After quenching in methanol and drying the polymer exhibited an  $\eta_{inh}$  of 0.4 dl/g, a Tg of initially

### 2.1.1.3 (Continued)

270°C, which increased to 312°C after cycling to 400°C, and a PST of 306 - 315°C. The polymer solution on the prepreg began to precipitate within 1.25 hours at 25°C temperature.

Test results from laminates made from each of the prepregs described above are shown in Tables 2 to 5. Laminate No. 1, 15 and 26 are respectively, the random copolymer, PPQ-I and PPQ-II. Each was made using the PMR process. Laminate No. 2, Table 2 is the random copolymer laminate which was made via PMR and vacuum impregnated on a flat table rather than drum wound.

Laminates 1 and 2 were cured one hour each at 336°C (636°F) and 454°C (850°F) under  $1.38 \times 10^6 \text{ N/m}^2$  (200 psi),  $\text{N}_2$  atmosphere. Laminates 15 and 26 were cured one hour each at 399°C (750°F) and 454°C (850°F) under  $1.38 \times 10^6 \text{ N/m}^2$  (200 psi).

The results of this study indicate that the PMR process, in general, is a very viable process and permits good fiber impregnation. The DMF solution of the random copolymer (1:3) and the PPQ-II provided a prepreg which was better impregnated and more uniform than those made from the more viscous m-cresol/xylene solutions. The resin did not show any tendency to flake off and the resulting composites demonstrated good properties.

Based on this evaluation, the PMR route does not appear practical for PPQ-I due to an apparent limited solubility of the polymer in NMP. Laminate No. 15 in Table 3, fabricated using PPQ-I, provided relatively poor properties. During impregnation on the rotating drum at ambient temperature, the resin began to precipitate from solution preventing formation of a uniform prepreg. The resulting prepreg was resin rich on one side with the resin exhibiting pronounced tendency to flake off.

TABLE 2 PROPERTIES OF POLYPHENYLQUINOXALINE GRAPHITE COMPOSITES

LAM. NO.	POLYMER	CURE CONDITIONS	FIBER VOLUME %	SPECIFIC GRAVITY	FLEXURE STRENGTH		FLEXURE MODULUS		INTERLAMINAR SHEAR STRENGTH	
					$10^8 \text{ N/m}^2$	$(10^3 \text{ PSI})$	$10^{10} \text{ N/m}^2$	$(10^6 \text{ PSI})$	$10^6 \text{ N/m}^2$	$(\text{PSI})$
					21°C	204°C	21°C	204°C	21°C	204°C
1	BaCo 1:3 via PFR	1 hr. each at 336°C and 454°C under $1.38 \times 10^6 \text{ N/m}^2$ $\text{N}_2$ atm	52.6	1.52	8.62 (125.0) 7.19 (104.2) 8.40 (121.8) 8.07 (117.0)	7.37 (106.9) 7.73 (112.1) 7.77 (112.6) 7.62 (110.5)	13.9 (20.2) 17.0 (24.7) 19.9 (28.9) 17.0 (24.6)	13.4 (19.5) 14.2 (20.6) 13.9 (20.2) 13.8 (20.1)	33.3 (4830) 31.7 (4590) 32.0 (4640) 32.3 (4690)	31.9 (4630) 33.4 (4840) — 32.7 (4740)
2			63.5	1.47	8.23 (119.4) 7.32 (106.2) 6.08 (88.1) 7.21 (104.6)	6.58 (95.5) 7.58 (109.9) 6.29 (91.2) 6.82 (98.9)	13.1 (19.0) 13.1 (19.0) 13.2 (19.2) 13.1 (19.1)	11.7 (17.0) 12.2 (17.7) 12.5 (18.1) 12.1 (17.6)	34.2 (4970) 28.3 (4110) 27.2 (3950) 29.9 (4340)	31.4 (4560) 28.8 (4180) 20.6 (2980) 26.9 (3910)
3	BiCo 1:3	1 hr. each at 336°C and 454°C under $2.07 \times 10^6 \text{ N/m}^2$	55.5	1.68	8.43 (122.2) 8.83 (128.1) 8.14 (118.0) 8.47 (122.8)	7.30 (105.8) 7.00 (101.5) 7.62 (110.5) 7.31 (105.9)	14.8 (21.4) 14.6 (21.1) 15.2 (22.0) 14.8 (21.5)	12.6 (18.3) 14.0 (20.3) 14.6 (21.1) 13.7 (19.9)	50.4 (7310) 46.3 (6720) 46.7 (6770) 47.8 (6930)	42.2 (6120) 42.1 (6100) 39.2 (5690) 41.2 (5970)
4			48.0	1.61	6.54 (94.9) 6.93 (100.5) 5.79 (84.0) 6.42 (93.1)	6.49 (94.1) 6.25 (90.6) 6.48 (94.0) 6.41 (92.9)	11.7 (17.0) 12.1 (17.5) 10.6 (15.3) 11.4 (16.6)	12.4 (18.0) 13.2 (19.1) 12.6 (18.2) 12.7 (18.4)	39.7 (5760) 37.7 (5470) 40.7 (5900) 39.4 (5710)	37.6 (5450) 38.1 (5530) 38.0 (5510) 37.9 (5500)
5		1 hr. each at 336°C and 454°C under $1.38 \times 10^6 \text{ N/m}^2$	60.0	1.65	7.12 (103.2) 6.01 (87.2) 7.41 (107.5) 6.85 (99.3)	6.83 (99.0) 6.61 (95.8) 6.23 (90.3) 6.55 (95.0)	14.6 (21.2) 12.6 (18.2) 13.4 (19.5) 13.5 (19.6)	12.6 (18.3) 13.6 (19.7) 11.9 (17.3) 12.7 (18.4)	31.0 (4490) 37.2 (5400) 34.9 (5060) 34.4 (4980)	35.3 (5120) 34.8 (5050) 28.3 (4110) 32.8 (4760)
6			60.0	1.60	7.85 (113.8) 8.68 (125.8) 8.67 (125.7) 8.40 (121.8)	5.61 (81.4) 5.50 (79.7) 7.28 (105.5) 6.13 (88.9)	12.1 (17.5) 12.7 (18.4) 12.6 (18.3) 12.5 (18.1)	11.6 (16.8) 10.1 (14.7) 12.6 (18.3) 11.4 (16.6)	37.0 (5360) 31.6 (4580) 42.1 (6100) 36.9 (5350)	30.1 (4360) 29.0 (4210) 33.1 (4800) 30.7 (4460)
7			51.0	1.52	5.77 (83.7) 5.43 (78.8) 6.23 (90.3) 5.81 (84.3)	6.32 (91.6) 5.90 (85.6) 5.53 (80.2) 5.92 (85.8)	10.9 (15.8) 9.9 (14.4) 11.1 (16.1) 10.6 (15.4)	10.9 (15.8) 10.2 (14.8) 11.0 (16.0) 10.7 (15.5)	32.8 (4750) 30.2 (4380) 33.3 (4830) 32.1 (4650)	26.9 (3900) 26.9 (3900) 26.4 (3830) 26.7 (3880)
8			49.0	1.55	6.04 (87.6) 5.01 (72.7) 6.39 (92.6) 5.81 (84.3)	3.97 (57.5) 4.83 (70.0) 6.41 (92.9) 5.07 (73.5)	9.1 (13.2) 8.9 (12.9) 9.9 (14.4) 9.3 (13.5)	8.1 (11.8) 9.0 (13.0) 10.4 (15.1) 9.2 (13.3)	32.6 (4730) 34.4 (4990) 29.2 (4230) 32.1 (4650)	31.0 (4500) 29.7 (4310) 26.8 (3880) 29.2 (4230)
9		1 hr. each at 399°C and 427°C under $1.38 \times 10^6 \text{ N/m}^2$ and $\text{N}_2$ atm	53.0	1.52	5.09 (73.8) 6.46 (93.6) 6.44 (93.4) 6.00 (86.9)	5.09 (73.8) 5.46 (79.2) 5.37 (77.9) 5.31 (77.0)	9.1 (13.2) 8.3 (12.0) 9.9 (14.4) 9.1 (13.2)	9.0 (13.0) 9.0 (13.1) 8.4 (12.2) 8.8 (12.8)	34.4 (4990) 31.4 (4550) 29.2 (4230) 31.7 (4590)	28.1 (4070) 25.1 (3640) 26.7 (3870) 26.6 (3860)
10			54.0	1.48	5.68 (82.4) 5.13 (74.4) 6.21 (90.0) 5.67 (82.3)	5.39 (78.1) 5.01 (72.6) 5.57 (80.7) 5.32 (77.1)	8.5 (12.3) 8.5 (12.3) 8.6 (12.5) 8.5 (12.4)	7.1 (10.3) 8.1 (11.8) 8.5 (12.3) 7.9 (11.5)	30.1 (4360) 29.2 (4230) 35.4 (5140) 31.6 (4580)	31.7 (4600) 27.5 (3990) 30.6 (4430) 29.9 (4340)

TABLE 3 PROPERTIES OF POLYPHENYLQUINOXALINE GRAPHITE COMPOSITES

LAM. NO	POLYMER	CURE CONDITIONS	FIBER VOLUME %	SPECIFIC GRAVITY	FLEXURE STRENGTH $10^8 \text{ N/m}^2$ ( $10^3 \text{ psi}$ )			FLEXURE MODULUS $10^{10} \text{ N/m}^2$ ( $10^6 \text{ psi}$ )			INTERLAMINAR SHEAR STRENGTH $10^6 \text{ N/m}^2$ (PSI)		
					21°C	204°C	316°C	21°C	204°C	316°C	21°C	204°C	316°C
11	BICo 1:3	1 hr at 399°C plus 2 hr at 427°C under $3.45 \times 10^6 \text{ N/m}^2$	62.0	1.54	7.88 (114.2)	7.47 (108.3)	3.94 (57.2)	14.0 (20.3)	13.2 (19.1)	10.9 (15.8)	36.6 (5300)	37.2 (5390)	23.2 (3360)
					8.45 (122.5)	6.90 (100.0)	4.96 (71.9)	13.7 (19.8)	10.9 (15.8)	11.7 (17.0)	36.5 (5290)	33.7 (4880)	21.7 (3150)
					6.93 (100.5)	7.70 (111.6)	5.82 (84.4)	12.2 (17.7)	13.6 (19.7)	13.0 (18.9)	37.6 (5450)	35.6 (5160)	17.8 (2580)
					7.75 (112.4)	7.35 (106.6)	4.91 (71.2)	13.3 (19.3)	12.6 (18.2)	11.9 (17.2)	36.9 (5350)	35.5 (5140)	20.9 (3030)
12			61.0	1.54	7.72 (112.0)	5.21 (75.6)	5.66 (82.0)	14.7 (21.3)	11.2 (16.2)	13.2 (19.1)	34.1 (4940)	33.4 (4850)	29.7 (4300)
					6.16 (89.3)	7.14 (103.6)	6.25 (90.6)	11.7 (16.9)	13.1 (19.0)	12.8 (18.6)	33.5 (4860)	34.9 (5060)	25.4 (3690)
					7.34 (106.5)	6.99 (101.3)	5.39 (78.1)	14.6 (21.1)	14.1 (20.5)	13.1 (19.0)	34.5 (5000)	31.9 (4630)	25.4 (3680)
					7.08 (102.6)	6.45 (93.5)	5.76 (83.6)	13.7 (19.8)	12.8 (18.6)	13.0 (18.9)	34.0 (4930)	33.4 (4850)	26.8 (3890)
13		1 hr at 399°C plus 2 hr at 427°C under $6.90 \times 10^6 \text{ N/m}^2$	61.0	1.53	8.94 (129.6)	6.37 (92.4)	2.94 (42.6)	15.0 (21.7)	14.1 (20.4)	6.7 (9.7)	38.1 (5530)	36.5 (5290)	16.6 (2400)
					5.37 (77.8)	7.90 (114.6)	5.14 (74.5)	14.1 (20.4)	14.1 (20.4)	11.9 (17.3)	38.1 (5530)	34.9 (5060)	27.0 (3910)
					7.87 (114.1)	7.79 (112.9)	2.72 (39.4)	14.9 (21.6)	16.5 (24.0)	5.9 (8.5)	40.7 (5900)	36.2 (5250)	15.5 (2250)
					7.39 (107.2)	7.35 (106.6)	3.60 (52.2)	14.6 (21.2)	14.9 (21.6)	8.2 (11.8)	39.0 (5650)	35.9 (5200)	19.7 (2850)
14			65.0	1.55	8.92 (129.3)	8.21 (119.0)	1.30 (18.8)	12.8 (18.5)	12.3 (17.9)	1.3 (1.9)	38.9 (5640)	36.0 (5220)	25.0 (3620)
					8.96 (129.9)	7.83 (113.6)	1.66 (24.0)	13.0 (18.9)	11.7 (17.0)	3.2 (4.7)	43.9 (6370)	38.3 (5560)	26.2 (3800)
					7.63 (110.7)	7.06 (102.3)	1.59 (23.0)	13.0 (18.9)	11.8 (17.1)	1.2 (1.7)	41.9 (6080)	37.5 (5440)	21.6 (3130)
					8.50 (123.3)	7.70 (111.6)	1.51 (21.9)	12.9 (18.8)	12.0 (17.3)	1.9 (2.8)	41.6 (6030)	37.3 (5410)	24.3 (3520)
15	PPQ I (PMR)	1 hr each at 399°C and 454°C under $1.38 \times 10^6 \text{ N/m}^2$	70.0	1.40	3.57 (51.8)	3.70 (53.7)	3.23 (46.9)	9.6 (13.9)	8.7 (12.6)	9.0 (13.1)	14.2 (2060)	23.2 (3360)	16.9 (2450)
					6.31 (91.5)	3.90 (56.6)	4.78 (69.3)	13.0 (18.8)	10.3 (15.0)	11.4 (16.6)	19.8 (2870)	20.5 (2970)	15.5 (2250)
					5.11 (74.1)	5.50 (79.7)	2.35 (34.1)	12.2 (17.7)	11.2 (16.3)	9.4 (13.6)	24.3 (3530)	17.9 (2600)	17.2 (2500)
					5.00 (72.5)	4.37 (63.3)	3.45 (50.0)	11.6 (16.8)	10.1 (14.6)	10.0 (14.4)	19.4 (2820)	20.5 (2980)	16.5 (2400)
16	BICo 1:3	8 hr at 371°C under $2.07 \times 10^6 \text{ N/m}^2$	61.5	1.52	7.95 (115.3)	5.46 (79.2)	4.21 (61.0)	11.8 (17.1)	10.0 (14.5)	8.7 (12.6)	29.2 (4240)	28.2 (4090)	14.7 (2130)
					7.99 (115.8)	5.97 (86.6)	3.54 (51.4)	12.6 (18.3)	10.6 (15.3)	8.8 (12.8)	37.2 (5400)	28.8 (4180)	13.9 (2010)
					7.60 (110.2)	6.66 (96.5)	2.61 (37.9)	12.5 (18.1)	10.9 (15.8)	6.9 (10.0)	30.0 (4350)	27.6 (4000)	13.4 (1940)
					7.85 (113.8)	6.03 (87.4)	3.46 (50.1)	12.3 (17.8)	10.5 (15.2)	8.1 (11.8)	32.2 (4660)	28.2 (4090)	14.0 (2030)
17			60.5	1.52	7.07 (102.5)	4.58 (66.4)	1.08 (15.6)	10.6 (15.3)	8.6 (12.5)	2.3 (3.4)	35.1 (5090)	32.6 (4730)	13.5 (1960)
					6.68 (96.9)	5.81 (84.3)	.97 (14.1)	11.0 (15.9)	10.7 (15.5)	.9 (1.3)	35.9 (5210)	23.9 (3460)	20.9 (3030)
					7.97 (115.5)	6.22 (90.2)	2.98 (43.2)	12.5 (18.1)	10.6 (15.4)	7.5 (10.9)	35.9 (5210)	26.1 (3790)	17.3 (2510)
					7.24 (105.0)	5.54 (80.3)	1.68 (24.3)	11.3 (16.4)	10.0 (14.5)	3.6 (5.2)	35.6 (5170)	27.5 (3990)	17.2 (2500)
18		4 hr at 371°C under $2.07 \times 10^6 \text{ N/m}^2$ and 4 hrs @ 371°C in N <sub>2</sub> (No pressure)	62.0	1.57	6.27 (90.9)	5.46 (79.2)	1.16 (18.6)	11.7 (17.0)	10.1 (14.7)	0.6 (0.9)	33.7 (4880)	30.5 (4420)	19.9 (2880)
					7.74 (112.2)	6.39 (92.6)	2.74 (42.6)	11.4 (16.5)	7.7 (11.2)	7.7 (11.1)	33.9 (4910)	29.1 (4220)	16.8 (2430)
					6.72 (97.5)	6.33 (91.8)	1.36 (22.5)	11.4 (16.5)	9.9 (14.3)	8.9 (12.9)	32.8 (4750)	26.3 (3820)	12.8 (1850)
					6.91 (100.2)	6.06 (87.9)	1.75 (25.4)	11.5 (16.7)	9.2 (13.4)	5.7 (8.3)	33.4 (4850)	28.6 (4150)	16.5 (2390)
19			63.0	1.56	6.30 (91.3)	6.20 (89.9)	1.28 (18.8)	10.5 (15.2)	9.9 (14.3)	2.7 (3.9)	34.6 (5020)	28.9 (4190)	16.7 (2420)
					6.30 (91.4)	6.21 (90.0)	1.34 (19.8)	10.8 (15.6)	10.3 (15.0)	8.1 (11.8)	35.1 (5090)	29.3 (4250)	17.0 (2460)
					7.38 (107.0)	6.23 (90.3)	1.79 (25.9)	11.9 (17.2)	9.9 (14.4)	7.2 (10.4)	33.1 (4800)	29.9 (4340)	15.3 (2220)
					6.66 (96.6)	6.21 (90.1)	1.47 (21.4)	11.0 (16.0)	10.0 (14.6)	6.0 (8.7)	34.3 (4970)	29.4 (4260)	16.3 (2370)
20		4 hr at 371°C under $2.07 \times 10^6 \text{ N/m}^2$ and 4 hr at 371°C in air (No pressure)	63.0	1.54	6.58 (95.4)	4.90 (71.0)	3.71 (53.8)	10.8 (15.7)	9.0 (13.0)	0.4 (0.6)	29.6 (4290)	26.6 (3860)	18.3 (2660)
					6.60 (95.7)	5.71 (82.8)	1.23 (19.5)	10.3 (15.0)	9.7 (14.0)	1.0 (1.5)	31.5 (4570)	27.0 (3910)	13.8 (2000)
					6.61 (95.8)	5.75 (83.4)	1.48 (21.3)	10.1 (14.7)	9.7 (14.1)	8.8 (12.7)	29.8 (4320)	27.8 (4030)	15.4 (2240)
					6.60 (95.6)	5.45 (79.1)	2.14 (31.3)	10.4 (15.1)	9.4 (13.7)	3.4 (4.9)	30.3 (4390)	27.1 (3930)	15.8 (2300)
21			63.2	1.53	5.90 (85.6)	4.90 (71.0)	1.28 (18.8)	11.1 (16.1)	9.0 (13.1)	9.9 (14.3)	32.1 (4650)	27.3 (3960)	15.5 (2250)
					6.74 (97.7)	6.25 (90.6)	2.94 (43.2)	10.3 (15.0)	10.3 (14.9)	.6 (0.9)	30.7 (4450)	29.2 (4230)	19.6 (2840)
					5.72 (82.9)	5.81 (84.2)	2.93 (42.6)	11.0 (16.0)	10.5 (15.2)	2.1 (3.1)	34.1 (4940)	27.8 (4030)	17.4 (2520)
					6.12 (88.7)	5.65 (81.9)	2.38 (34.7)	10.8 (15.7)	9.9 (14.4)	4.2 (6.1)	32.3 (4680)	28.1 (4070)	17.5 (2540)
22/23		2 hrs @ 371°C and 2 hrs at 399°C under $2.07 \times 10^6 \text{ N/m}^2$ and 4 hr at 427°C in N <sub>2</sub> (No pressure)	61.5 / 60.5	- / 1.61	BLEW DURING POST CURE AT 800°F, NOT TESTED								

TABLE 4 PROPERTIES OF POLYPHENYLQUINOXALINE GRAPHITE COMPOSITES

LAM NO.	POLYMER	CURE CONDITIONS	FIBER VOLUME %	SPECIFIC GRAVITY	FLEXURE STRENGTH $10^8 \text{ N/m}^2$ ( $10^3 \text{ PSI}$ )			FLEXURE MODULUS $10^{10} \text{ N/m}^2$ ( $10^6 \text{ PSI}$ )			INTERLAMINAR SHEAR STRENGTH $10^6 \text{ N/m}^2$ ( $\text{PSI}$ )		
					21°C	204°C	316°C	21°C	204°C	316°C	21°C	204°C	316°C
24	PPQ-II (PMR)	1 hr. at 371°C and 1 hr. at 427°C under $1.38 \times 10^6 \text{ N/m}^2$	62.0	1.62	8.33 (120.8) 8.87 (128.6) 6.21 (90.6) 7.81 (113.3)	7.35 (106.6) 7.82 (113.4) 6.72 (97.4) 7.30 (105.8)	3.70 (53.6) 2.23 (32.4) 2.23 (32.4) 2.72 (39.5)	16.2 (23.5) 15.2 (22.1) 14.6 (21.2) 15.4 (22.3)	15.3 (21.8) 14.3 (20.8) 14.2 (20.6) 14.5 (21.1)	9.3 (13.5) 1.9 (2.8) 1.6 (2.4) 4.3 (6.2)	38.5 (5580) 31.7 (4600) 37.8 (5480) 36.0 (5220)	31.7 (4600) 31.5 (4570) 34.1 (4940) 32.4 (4700)	15.1 (2190) 11.3 (1640) 15.6 (2260) 14.0 (2030)
25				1.62	8.28 (120.1) 8.52 (123.6) 7.13 (103.4) 7.98 (115.7)	8.31 (120.5) 5.69 (82.5) 7.98 (115.7) 7.34 (106.2)	2.24 (32.5) 2.19 (31.7) 3.19 (46.3) 2.54 (36.8)	15.2 (22.0) 16.4 (23.8) 16.0 (23.2) 15.9 (23.0)	16.0 (23.2) 14.9 (21.6) 15.2 (22.1) 15.4 (22.3)	3.0 (4.3) 2.6 (3.8) 9.7 (14.1) 5.1 (7.4)	38.4 (5570) 33.7 (4880) 38.6 (5600) 36.9 (5350)	31.2 (4520) 25.6 (3710) 29.9 (4340) 28.9 (4190)	21.4 (3100) 11.3 (1640) 12.5 (1810) 15.1 (2180)
26		1 hr. at 399°C and 1 hr. at 454°C under $1.38 \times 10^6 \text{ N/m}^2$	61.0	1.61	8.30 (120.4) 9.26 (134.3) 7.01 (101.6) 8.19 (118.8)	7.33 (106.4) 8.71 (126.3) 6.34 (91.9) 7.46 (108.2)	3.52 (51.1) 2.52 (36.5) 4.41 (63.9) 3.48 (50.5)	15.9 (23.1) 16.5 (23.9) 15.8 (22.9) 16.1 (23.3)	16.0 (23.2) 15.9 (23.0) 15.1 (21.9) 15.7 (22.7)	11.0 (15.9) 5.9 (8.5) 10.1 (14.7) 9.0 (13.0)	42.1 (6100) 41.0 (5950) 34.8 (5040) 39.3 (5700)	33.2 (4810) 31.1 (4510) 30.8 (4460) 31.7 (4590)	26.8 (3880) 25.4 (3690) 19.4 (2820) 23.9 (3460)
27				1.61	8.17 (118.5) 9.40 (136.4) 9.01 (130.6) 8.86 (128.5)	7.54 (109.4) 9.65 (139.9) 7.82 (113.4) 8.34 (120.9)	5.74 (83.3) 4.01 (58.1) 4.60 (66.7) 4.78 (69.4)	14.0 (20.3) 15.3 (22.2) 15.1 (21.9) 14.8 (21.5)	12.8 (18.6) 14.1 (20.4) 13.9 (20.2) 13.6 (19.7)	13.2 (19.2) 9.5 (13.8) 10.1 (14.7) 11.0 (15.9)	39.8 (5770) 34.6 (5020) 41.3 (5990) 38.6 (5590)	37.2 (5390) 34.1 (4950) 38.3 (5550) 36.5 (5300)	22.7 (3290) 23.1 (3350) 20.6 (2980) 22.1 (3210)
28		2 hrs. at 427°C under $3.45 \times 10^6 \text{ N/m}^2$	62.0	1.68	8.64 (125.3) 9.06 (131.4) 10.30 (149.4) 9.34 (135.4)	8.95 (129.8) 8.79 (127.4) 8.66 (125.6) 8.80 (127.6)	5.98 (86.7) 6.01 (87.1) 4.89 (70.9) 5.63 (81.6)	15.2 (22.1) 15.2 (22.1) 15.4 (22.4) 15.3 (22.2)	15.4 (22.3) 15.0 (21.7) 15.2 (22.1) 15.2 (22.0)	13.4 (19.4) 13.0 (18.9) 12.1 (17.5) 12.8 (18.6)	46.0 (6670) 49.4 (7170) 39.0 (5650) 44.8 (6500)	41.3 (5990) 38.8 (5630) 37.4 (5430) 39.2 (5680)	24.6 (3570) 21.9 (3170) 25.9 (3760) 24.1 (3500)
29				1.68	8.28 (120.1) 9.42 (136.6) 9.36 (135.8) 9.02 (130.8)	8.32 (120.7) 7.08 (102.7) 8.34 (121.0) 7.92 (114.8)	4.63 (67.1) 5.43 (78.7) 4.88 (70.7) 4.98 (72.2)	15.2 (22.0) 16.6 (24.0) 15.0 (21.7) 15.6 (22.6)	14.1 (20.4) 14.4 (20.9) 14.9 (21.6) 14.5 (21.0)	11.5 (16.7) 12.1 (17.5) 11.4 (16.6) 11.7 (16.9)	38.9 (5640) 40.4 (5860) 39.6 (5740) 39.6 (5750)	37.4 (5430) 34.6 (5020) 33.9 (4910) 35.3 (5120)	24.7 (3580) 22.9 (3320) 25.8 (3740) 24.5 (3550)
30		2 hrs. at 454°C under $3.45 \times 10^6 \text{ N/m}^2$	63.0	1.71	9.54 (138.3) 9.81 (142.2) 11.75 (170.4) 10.36 (150.3)	9.55 (138.5) 9.94 (144.1) 9.85 (142.8) 9.78 (141.8)	5.51 (79.9) 5.04 (73.1) 4.95 (71.8) 5.17 (74.9)	15.7 (22.8) 15.8 (22.9) 16.0 (23.2) 15.8 (23.0)	15.7 (22.7) 18.5 (26.8) 15.7 (22.8) 16.6 (24.1)	13.8 (20.0) 11.2 (16.3) 11.0 (16.0) 12.0 (17.4)	49.9 (7230) 45.4 (6590) 46.6 (6750) 47.3 (6860)	40.9 (5930) 41.0 (5940) 41.9 (6070) 41.2 (5980)	27.7 (4010) 24.2 (3510) 27.2 (3940) 26.3 (3820)
31				1.71	9.74 (141.2) 10.09 (146.3) 9.86 (143.0) 9.90 (143.5)	9.03 (131.0) 10.13 (147.0) 9.37 (135.8) 9.51 (137.9)	4.94 (71.7) 4.65 (67.4) 4.81 (69.8) 4.80 (69.6)	15.6 (22.6) 16.4 (23.8) 15.5 (22.5) 15.8 (23.0)	15.2 (22.0) 16.2 (23.5) 15.5 (22.5) 15.6 (22.7)	13.2 (19.2) 11.4 (16.5) 12.8 (18.5) 12.5 (18.1)	55.5 (8050) 52.6 (7620) 51.2 (7430) 53.1 (7700)	43.4 (6300) 38.9 (5640) 40.3 (5850) 40.9 (5930)	33.7 (4890) 21.4 (3110) 23.4 (3400) 26.2 (3800)
32		2 hrs. at 454°C under $2.07 \times 10^6 \text{ N/m}^2$	60.0	1.66	9.27 (134.4) 11.08 (160.7) 11.86 (164.7) 10.57 (153.3)	2.78 (40.3) 9.30 (134.8) 8.43 (122.3) 6.84 (99.1)	2.28 (33.1) 4.21 (61.0) 4.23 (61.3) 3.57 (51.8)	14.7 (21.3) 15.2 (22.0) 15.7 (22.8) 15.2 (22.0)	6.3 (9.2) 11.8 (17.1) 13.7 (19.9) 10.6 (15.4)	3.2 (4.7) 4.8 (7.0) 7.7 (11.2) 5.3 (7.6)	37.0 (5370) 25.4 (3690) 33.9 (4910) 32.1 (4660)	29.9 (4340) 29.8 (4320) 26.0 (3770) 28.6 (4140)	13.4 (1940) 16.5 (2390) 17.0 (2460) 15.6 (2260)
33				1.66	9.84 (142.7) 11.15 (161.7) 8.86 (128.7) 9.96 (144.4)	7.35 (106.6) 6.88 (99.8) 8.14 (118.0) 7.46 (108.1)	2.74 (39.7) 3.63 (52.6) 3.64 (52.8) 3.34 (48.4)	14.9 (21.6) 14.2 (20.6) 13.8 (20.0) 14.3 (20.7)	14.3 (20.7) 14.0 (20.3) 14.3 (20.7) 14.2 (20.6)	6.8 (9.8) 7.9 (11.5) 7.9 (11.4) 7.5 (10.9)	35.2 (5100) 34.9 (5060) 36.7 (5320) 35.6 (5160)	30.6 (4430) 30.1 (4370) 34.5 (5000) 31.7 (4600)	17.0 (2470) 15.7 (2280) 16.5 (2390) 16.4 (2380)
34		4 hrs. at 454°C under $3.45 \times 10^6 \text{ N/m}^2$	61.0	1.70	9.43 (136.7) 9.07 (131.5) 9.32 (135.1) 9.27 (134.4)	7.99 (115.8) 7.50 (108.7) 8.49 (123.1) 7.99 (115.9)	5.64 (81.8) 4.27 (61.9) 5.38 (78.0) 5.10 (73.9)	14.6 (21.2) 14.2 (20.6) 14.6 (21.1) 14.5 (21.0)	14.8 (21.5) 13.3 (19.3) 13.7 (19.9) 14.0 (20.2)	11.5 (16.7) 10.2 (14.8) 11.3 (16.4) 11.0 (16.0)	42.9 (6220) 35.3 (5120) 40.9 (5930) 39.7 (5760)	30.1 (4370) 35.7 (5180) 26.5 (3840) 30.8 (4460)	20.1 (2920) 25.0 (3630) 23.2 (3360) 22.8 (3300)
35				1.70	8.55 (124.0) 9.85 (142.8) 8.66 (125.8) 9.03 (130.9)	8.00 (116.0) 8.03 (116.4) 7.38 (107.0) 7.80 (113.1)	6.24 (90.5) 5.81 (84.3) 3.93 (57.0) 5.33 (77.3)	13.8 (20.0) 14.8 (21.5) 12.9 (18.7) 13.8 (20.1)	13.8 (20.0) 13.7 (19.9) 13.2 (19.2) 13.6 (19.7)	12.0 (17.4) 10.1 (14.6) 10.8 (15.6) 10.9 (15.9)	36.6 (5300) 32.3 (4690) 40.7 (5900) 36.5 (5300)	29.9 (4330) 32.1 (4650) 27.4 (3970) 29.8 (4320)	18.8* (2720) 22.9 (3320) 23.2 (3370) 21.6 (3140)

TABLE 5 PROPERTIES OF RANDOM COPOLYMER GRAPHITE COMPOSITES

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE °C (°F)	FLEXURAL PROPERTIES		INTERLAMINAR SHEAR STRENGTH $10^6 \text{ N/m}^2$ (psi)
	TIME HRS.	TEMPERATURE °C (°F)		STRENGTH $10^8 \text{ N/m}^2$ ( $10^3 \text{ psi}$ )	MODULUS $10^{10} \text{ N/m}^2$ ( $10^6 \text{ psi}$ )	
1 *	200	316 (600)	316 (600)	5.06 (73.4) 4.65 (67.4) 4.86 (70.4)	9.7 (14.0) 9.7 (14.0) 9.7 (14.0)	24.8 (3590) 25.5 (3700) 25.1 (3650)
	500			3.25 (47.1) 2.97 (43.1) 3.11 (45.1)	21.1 (30.6) 8.6 (12.5) 14.9 (21.6)	11.5 (1670) 20.6 (2980) 16.0 (2330)
2 *	200			5.46 (79.1) 5.31 (77.0) 5.38 (78.1)	11.0 (16.0) 10.2 (14.8) 10.6 (15.4)	17.9 (2600) 29.0 (4200) 23.4 (3400)
	500			3.01 (43.6) 3.75 (54.4) 3.38 (49.0)	8.3 (12.0) 10.3 (14.9) 9.3 (13.5)	11.7 (1700) 12.3 (1780) 12.0 (1740)

\* Polymer batch PH-1-244

Laminate Cure: 1 hr. each at 336°C and 454°C under  $1.38 \times 10^6 \text{ N/m}^2$  and  $\text{N}_2$  atm.

Fiber Volume: 52.6%



### 2.1.3 (Continued)

The principal advantage offered by the PMR approach is a lower viscosity solution which appears to provide better wetting of the fibers. A minor disadvantage would be the limited shelf-life of the solution. However, this is not considered to be a serious deficiency in most cases.

Comparing the drum wound and the vacuum impregnated prepreg (laminate 1 and 2) no significant differences in mechanical properties were noted between the two. The drum wound prepreg was more uniform and resulting composite had better fiber distribution and lower void content (Figures 1 and 2). Drum wound impregnation was chosen as the preferred method of impregnation.

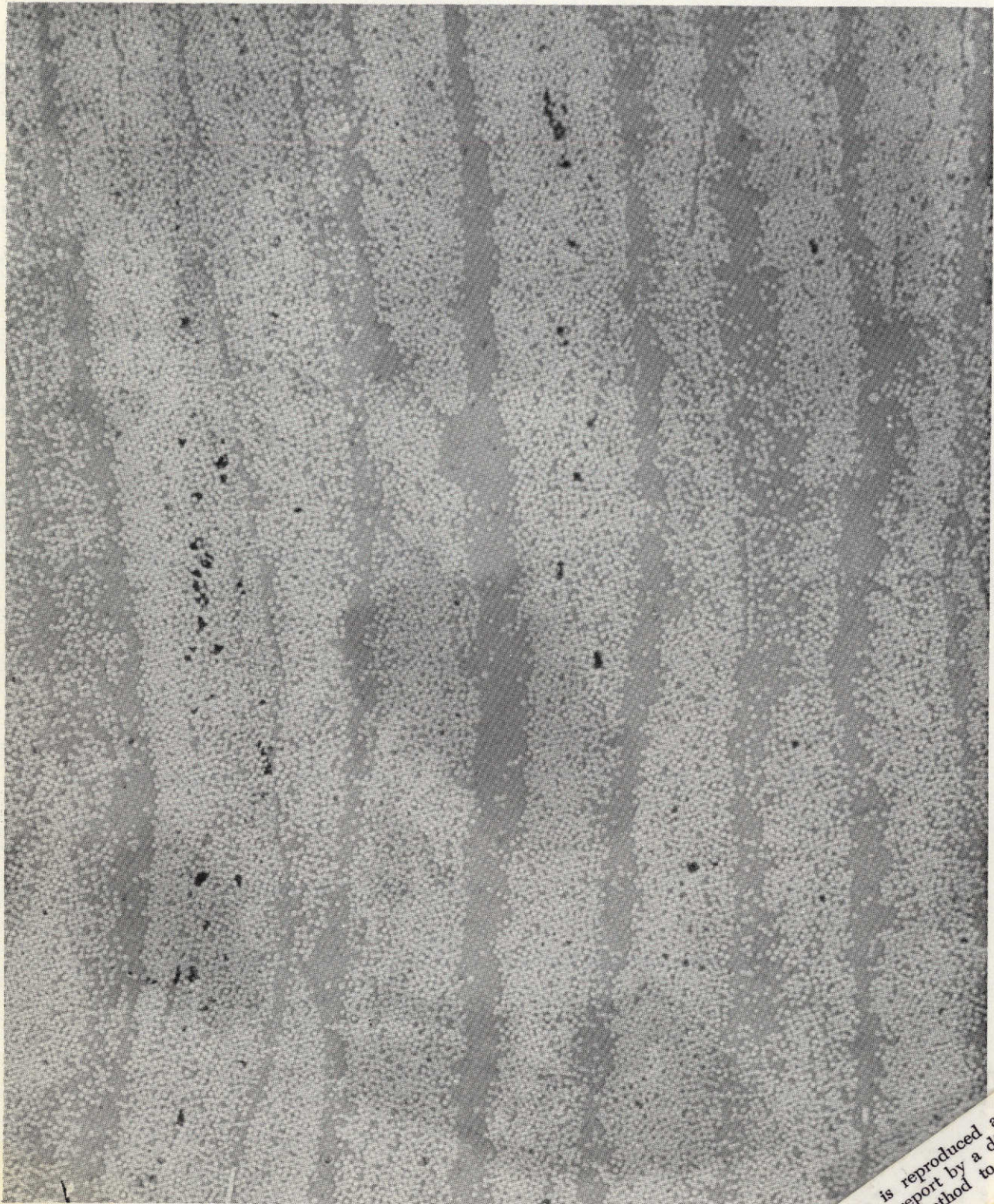
## 2.2 Resin Content Studies

To investigate the influence of resin content on laminate properties a series of laminates were made at 50% and 60% fiber volumes using the block copolymer 1:3 (Reference 1). Duplicate laminates (Nos. 5-8, Table 2) were made at each fiber volume. As shown in Table 2, the higher fiber volume laminates did translate better mechanical properties as would be expected. There was some concern that the brittle PPQ resin may result in lower interlaminar shear properties at the higher fiber volume.

Two additional laminates (No. 9 and 10, Table 2) were made at a  $V_f = 50\%$  under different processing conditions to determine if the properties would be influenced significantly by the change. Comparing the results of laminates 9 and 10 to 7 and 8 shows no influencing change.

Laminates for the remainder of the program were designed to have a  $V_f = 60\%$ .





*Figure 1: Cross Section of Laminate No. 1 (X65)*

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*Figure 2: Cross Section of Laminate No. 2 (X65)*

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Curing conditions were investigated on two PPQ polymers in an attempt to increase their elevated temperature performance and thermal aging characteristics. Six different cure/post-cure combinations were tried on the BlCo (1:3) polymer and an additional six combinations on PPQ-II as shown in Tables 3 and 4. Each laminate was tested for flexural strength, modulus, and interlaminar shear strength at 21°C, 204°C and 316°C. The results of these tests are shown in Tables 3 and 4. The cure cycle of 2 hours at 427°C (800°F) under  $1.38 \times 10^6 \text{ N/m}^2$  (200 psi) established previously (Reference 1) was used as the baseline in selecting the new cure cycles.

Based on these values a cure cycle of 1 hour each at 336°C (636°F) and 454°C (850°F) under  $2.07 \times 10^6 \text{ N/m}^2$  (300 psi) was chosen for the 1:3 BlCo polymer and 2 hours at 454°C (850°F) under  $2.07 \times 10^6 \text{ N/m}^2$  (300 psi) for the PPQ-II polymer.

A cross-sectional photograph of each laminate cure condition, with the exception of laminates 22 and 23, is shown in Figures 4-14. Laminates 22 and 23 blew during postcuring. Figures 15-16, and 17-18 are typical electron scanning photomicrographs of failed flexural specimens of BlCo (1:3) and PPQ-II polymers respectively.

In addition to performing flexural and ILS property determinations, creep and isothermal aging tests were conducted on laminates from each polymer. The results are presented in Figure 3 and Table 6 respectively. The creep tests were conducted using flexural specimens under a constant single point load condition at 316°C (+600°F).

The isothermal aging tests were run at 316°C in air for a minimum of 400 hours exposure (Table 6).

Laminates are further described in Tables 7-9.

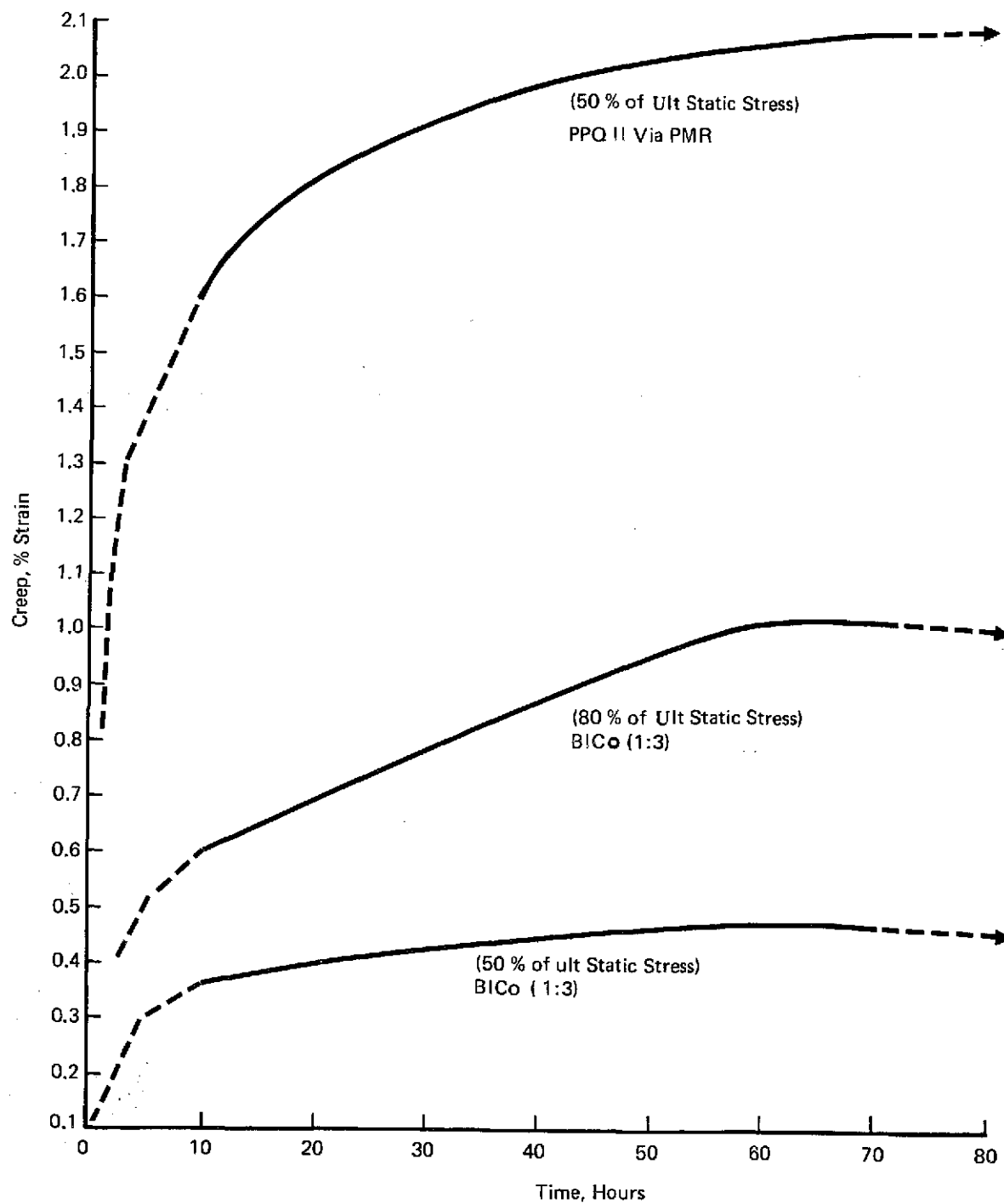


Figure 3 : Flexural Creep Properties of PPQ Graphite Composites at 316°C (600°F)



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*Figure 4: Cross Section of Laminate No. 11 (X65)*



*Figure 5: Cross Section of Laminate No. 13 (X65)*



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*Figure 6: Cross Section of Laminate No. 16 (X65)*



*Figure 7: Cross Section of Laminate No. 18 (X65)*



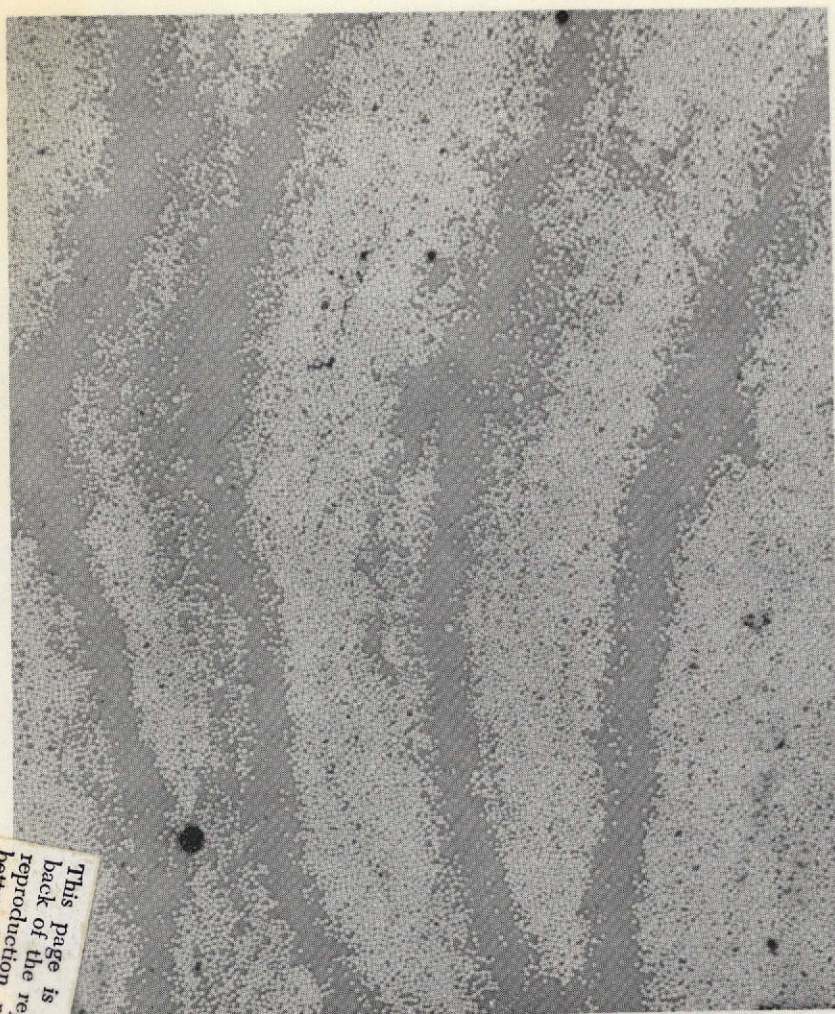


Figure 8: Cross Section of Laminate No. 20 (X65)



Figure 9: Cross Section of Laminate No. 24 (X65)

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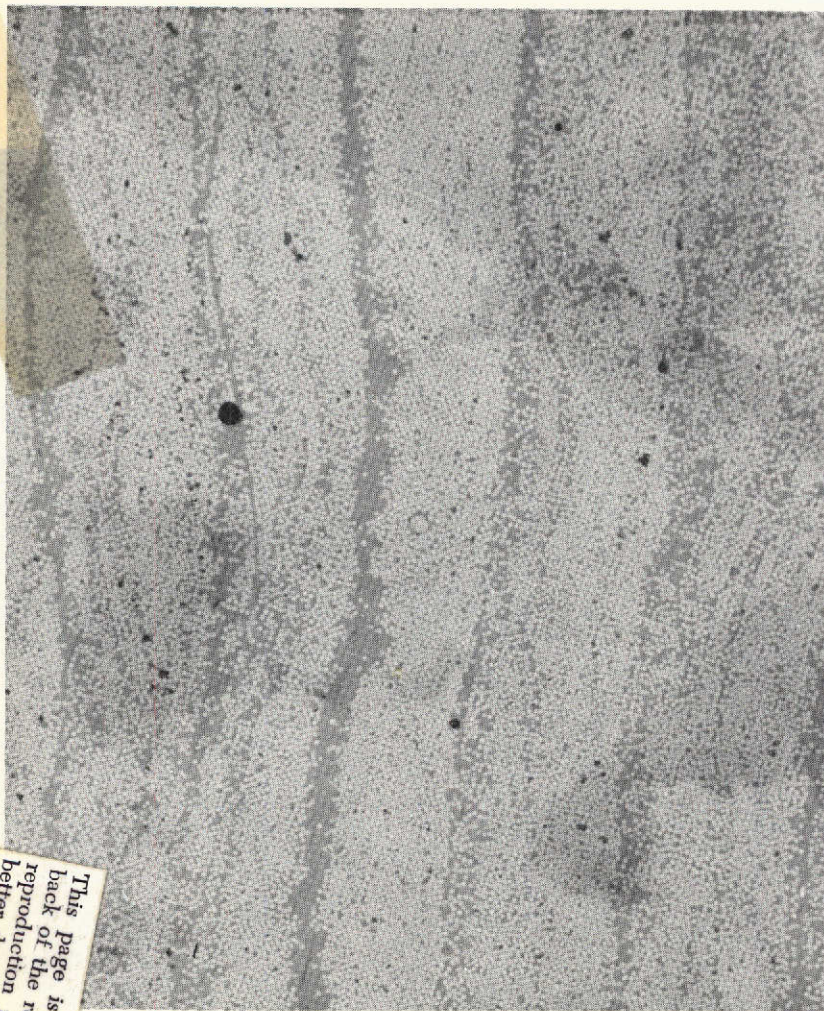


Figure 10: Cross Section of Laminate No. 26 (X65)



Figure 11: Cross Section of Laminate No. 28 (X65)

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Figure 12: Cross Section of Laminate No. 30 (X65)

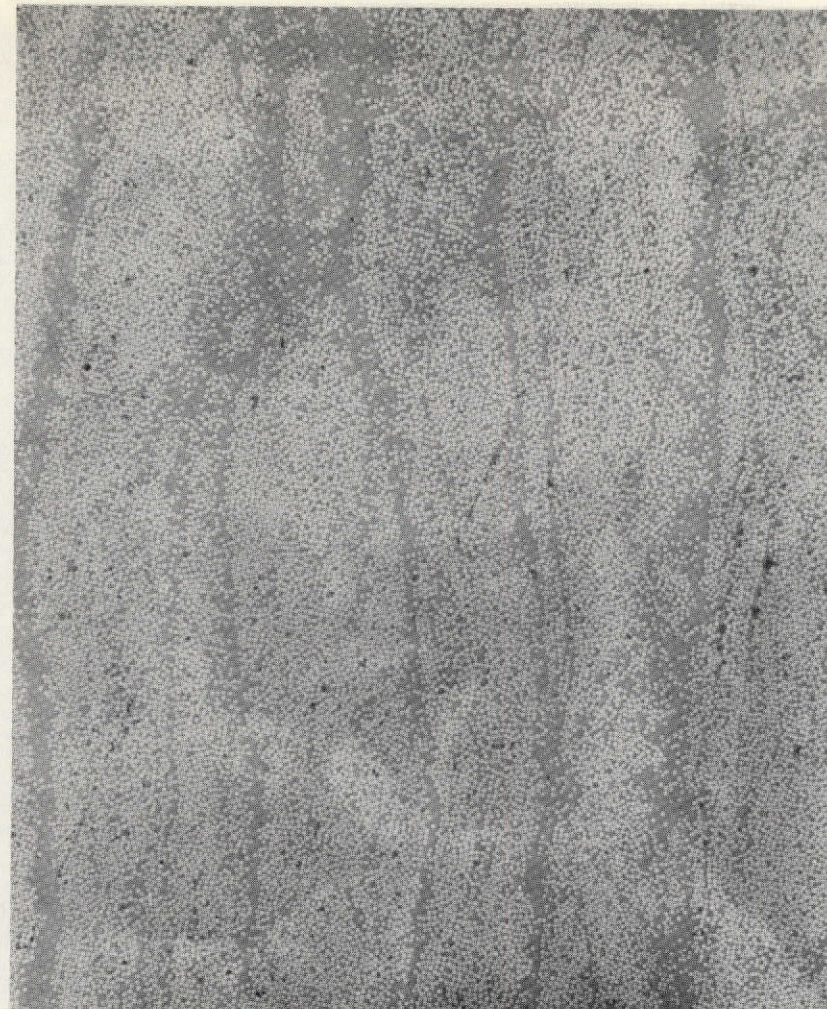


Figure 13: Cross Section of Laminate No. 32 (X65)

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*Figure 14: Cross Section of Laminate No. 34 (X65)*

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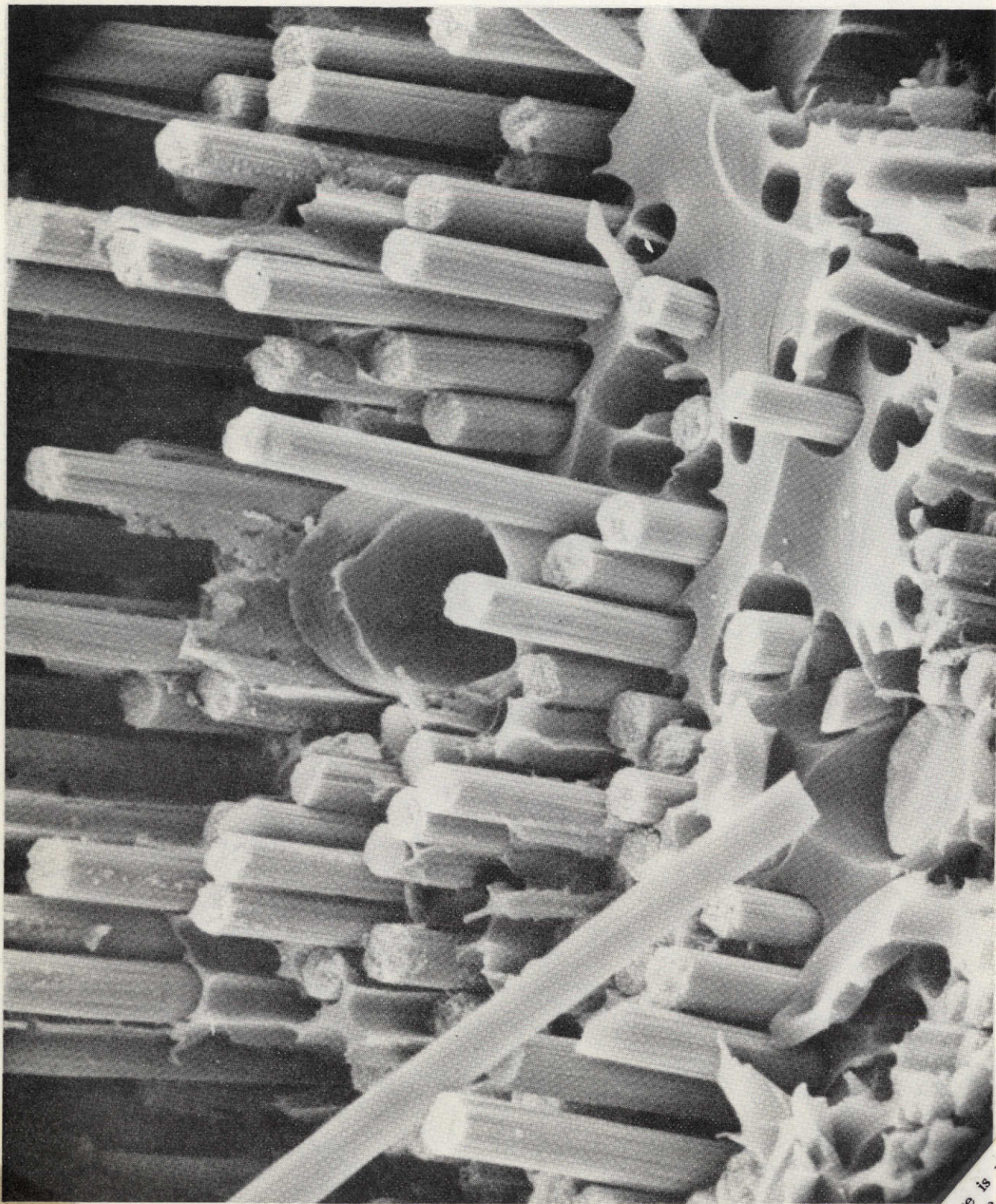
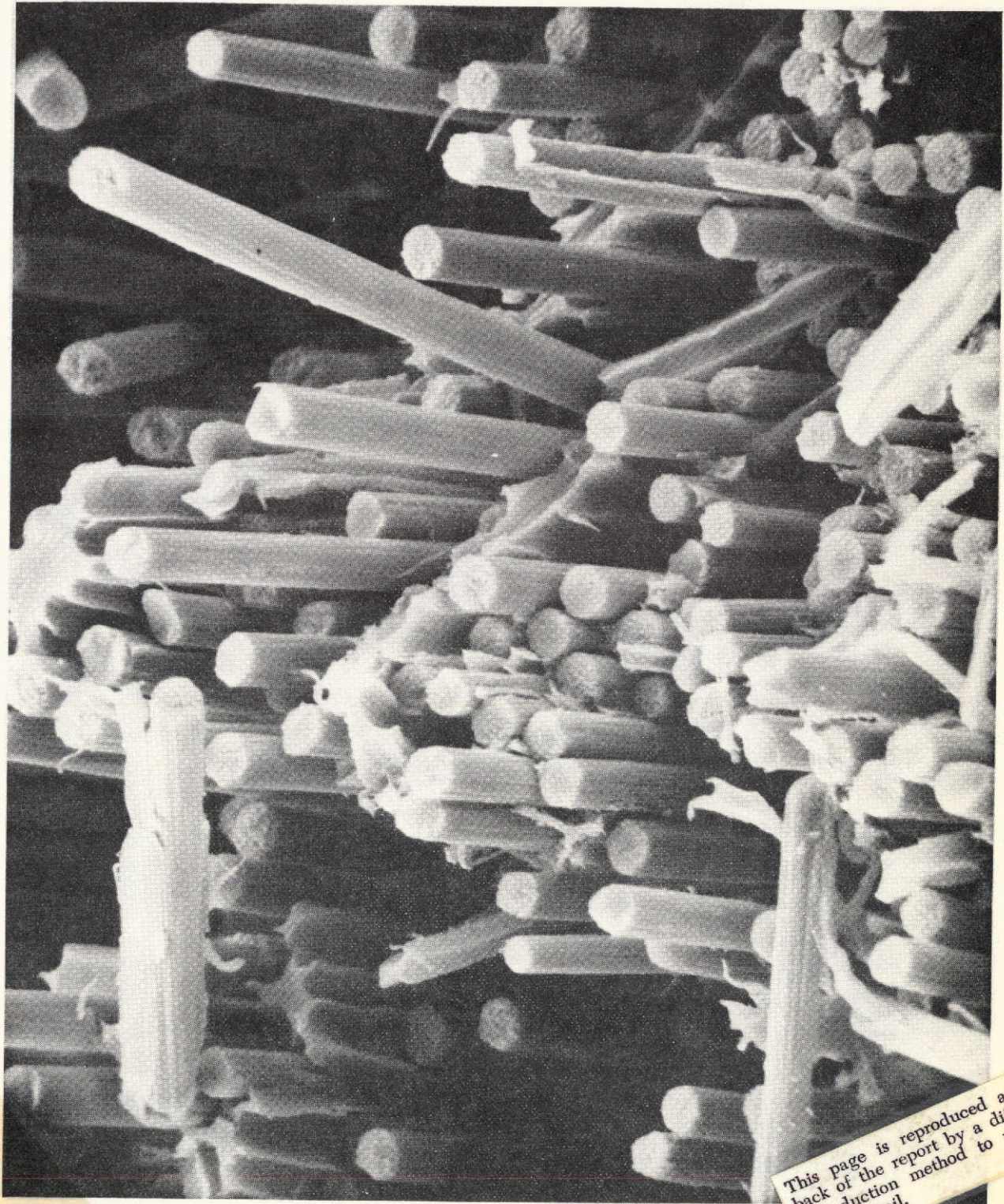


Figure 15: Electron Photomicrograph of Flexural Test Failure Area  
Laminate No. 18 (X600)

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Figure 16: Electron Photomicrograph of Flexural Test Failure Area  
Laminate No. 16 (X600)



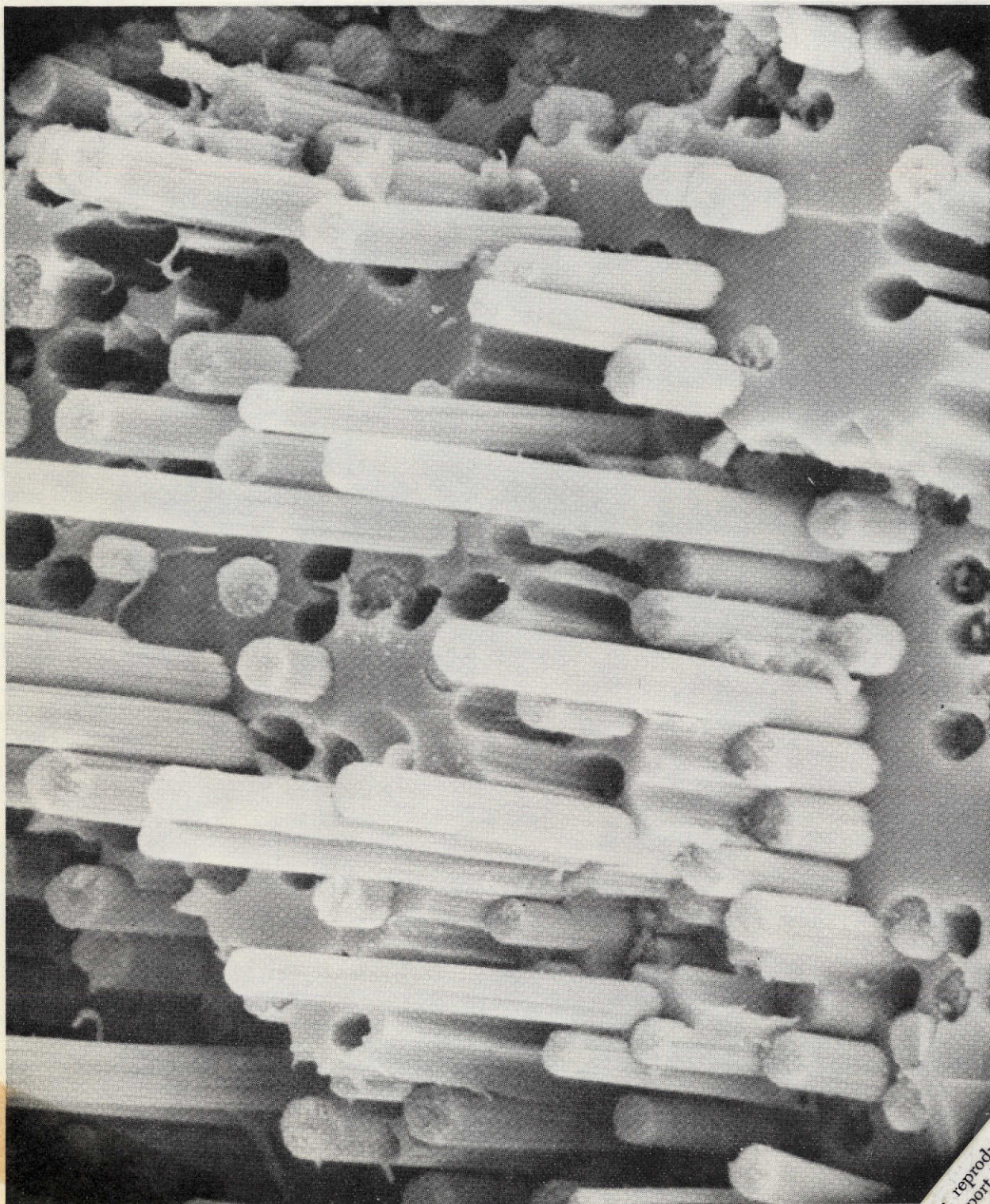


Figure 17: *Electron Photomicrograph of Flexural Test Failure Area  
Laminate No. 32 (X600)*

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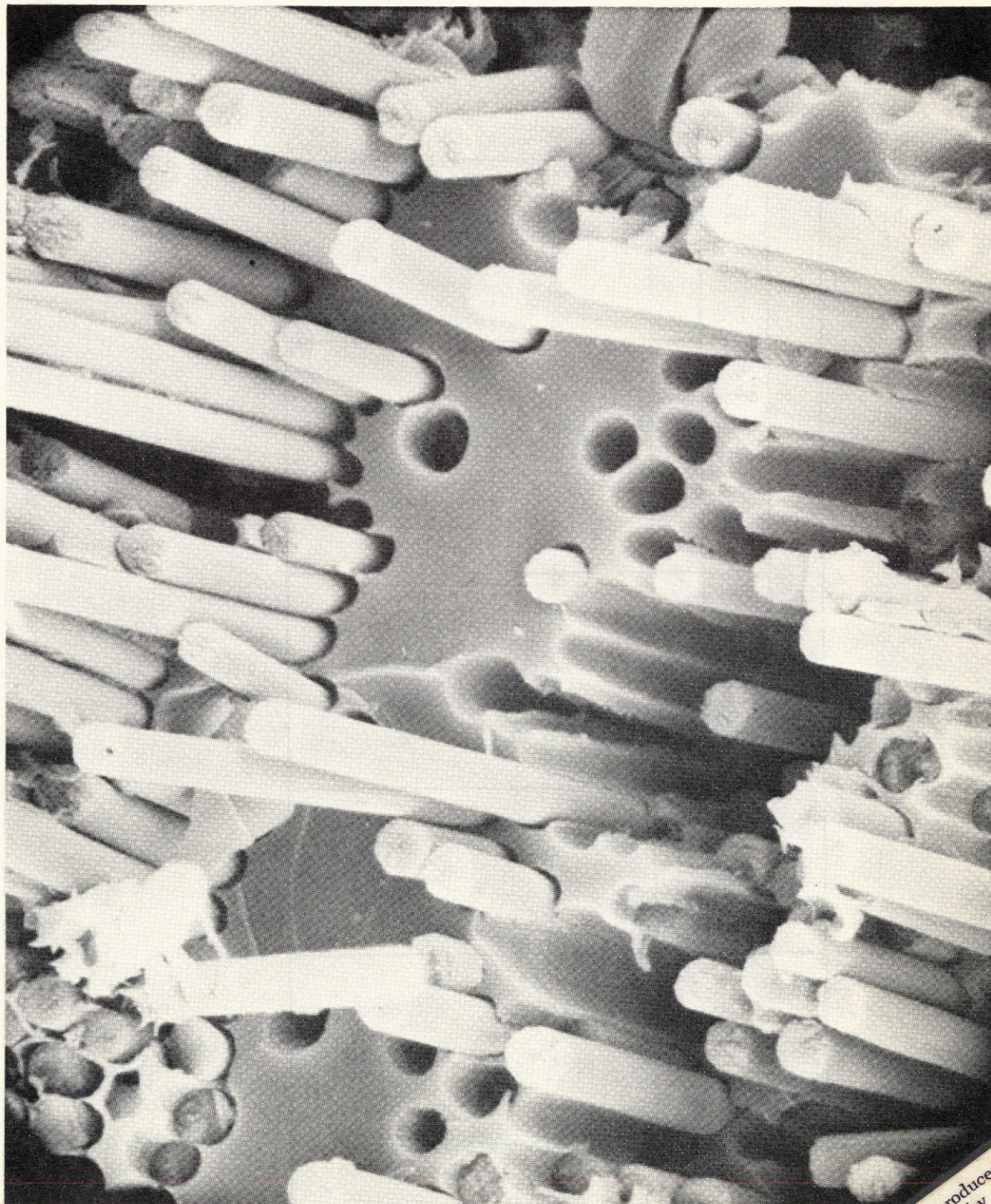


Figure 18: Electron Photomicrograph of Flexural Test Failure Area  
Laminate No. 30 (X600)

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Table 6 ISOTHERMAL AGING OF PPQ-II AND B1Co (1:3)  
GRAPHITE COMPOSITES AT 316°C (600°F) AND 371°C (700°F)

HOURS AGING	WEIGHT LOSS (%)			
	PPQ-II AGING TEMPERATURE °C		B1Co (1:3) AGING TEMPERATURE °C	
	316	371	316	371
100	2.35	6.95	2.21	7.20
200	3.50	13.75	3.20	14.10
300	4.40	24.00	4.15	22.14
400	5.85	31.00	5.60	30.00
500	7.10	33.00	6.95	32.15



TABLE 7 LAMINATE DESCRIPTION

LAMINATE NUMBER	POLYMER	POLYMER ITEM NO. *	PREPREG VOLATILE, %	THICKNESS		SPECIFIC GRAVITY
				mm	INCHES	
1	RaCo (1:3) via PMR ↓	1	2.10	3.35 - 3.49	.1320 - .1375	1.52
2		↓	0.73	2.69 - 2.74	.1060 - .1080	1.47
3	BlCo (1:3) ↓	2	1.20	2.38 - 2.52	.0936 - .0994	1.68
4		↓	0.78	3.16 - 3.28	.1244 - .1292	1.61
5	↓	↓	0.75	2.51 - 2.55	.0990 - .1004	1.65
6			1.70	2.40 - 2.56	.0946 - .1008	1.60
7			1.20	2.72 - 2.79	.1071 - .1098	1.52
8			1.60	2.70 - 2.88	.1064 - .1132	1.55
9			1.70	2.83 - 3.14	.1116 - .1238	1.52
10			1.40	2.95 - 3.14	.1162 - .1235	1.48
11			1.10	2.31 - 2.49	.0910 - .0980	1.54
12			1.40	2.47 - 2.57	.0971 - .1010	1.54
13			0.80	2.34 - 2.49	.0920 - .0980	1.53
14			1.20	2.90 - 2.92	.1141 - .1150	1.55
15	PPQ I via PMR	4	2.20	2.34 - 2.69	.0923 - .1061	1.40

\* SEE TABLE 1

TABLE 8 LAMINATE DESCRIPTION

LAMINATE NUMBER	POLYMER	POLYMER ITEM NO. *	PREPREG VOLATILE, %	THICKNESS		SPECIFIC GRAVITY
				mm	INCHES	
16	B1Co (1:3)	2	1.20	2.87 - 2.95	.1130 - .1160	1.52
17	↓	↓	1.80	2.97 - 3.10	.1170 - .1220	1.52
18	↓	↓	0.10	3.02 - 3.12	.1190 - .1230	1.57
19	↓	↓	0.20	2.92 - 3.10	.1150 - .1220	1.56
20	↓	↓	0.20	3.05 - 3.28	.1200 - .1290	1.54
21	↓	↓	0.10	2.74 - 2.97	.1080 - .1170	1.53
22	↓	↓	2.40	-	-	-
23	↓	↓	2.20	2.34 - 2.69	.0923 - .1061	1.61
24	PPQ II via PMR	6	1.20	2.29 - 2.54	.0900 - .1000	1.62
25	↓	↓	1.20	2.29 - 2.54	.0900 - .1000	1.62
26	↓	↓	1.80	2.16 - 2.54	.0850 - .1000	1.61
27	↓	↓	1.80	2.16 - 2.54	.0850 - .1000	1.61
28	↓	↓	0.40	2.34 - 2.51	.0920 - .0990	1.68
29	↓	↓	0.40	2.34 - 2.51	.0920 - .0990	1.68
30	↓	↓	0.60	2.36 - 2.39	.0930 - .0940	1.71

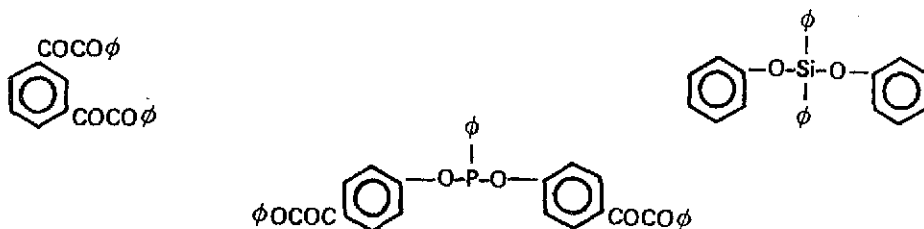
\* SEE TABLE 1

TABLE 9 LAMINATE DESCRIPTION

LAMINATE NUMBER	POLYMER	POLYMER ITEM NO. *	PREPREG VOLATILE, %	THICKNESS		SPECIFIC GRAVITY
				mm	INCHES	
31	PPQ-II via PMR	6	0.60	2.36 - 2.39	.0930 - .0940	1.71
32	↓	↓	1.10	2.54 - 2.67	.1000 - .1050	1.66
33	↓	↓	1.10	2.54 - 2.67	.1000 - .1050	1.66
34	↓	↓	1.30	2.51 - 2.57	.0990 - .1010	1.70
35	↓	↓	1.30	2.51 - 2.57	.0990 - .1010	1.70
36	TAB/m-BPGB	3	1.38	2.44 - 2.64	.0960 - .1040	1.61
37	B1Co (1:3) End CAPPED	5	1.40	2.44 - 2.67	.0960 - .1050	1.57
38 a+b	↓	↓	1.20	2.61 - 2.92	.1030 - .1150	1.53
39	TAB/m-BPGB	3	1.31	2.61 - 2.89	.1030 - .1140	1.62

\* SEE TABLE 1

The original objectives in Task II were to synthesize and characterize polyphenylquinoxaline polymers from 3,3',4,4'-tetraaminobenzophenone (TAB) and the following tetracarbonyl compounds.



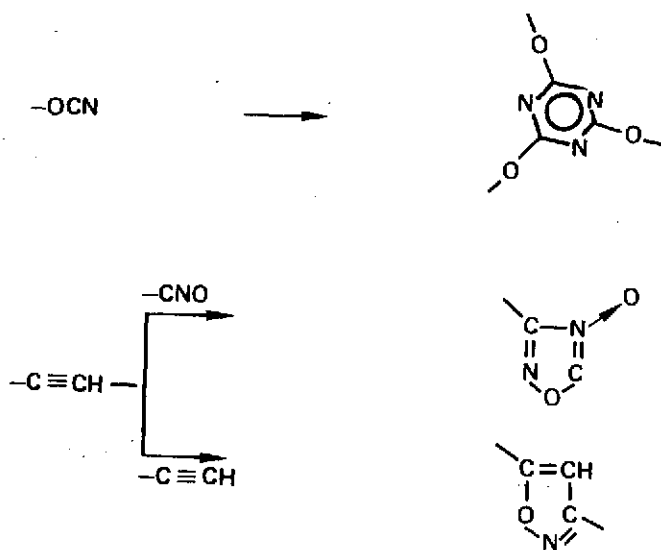
These objectives were modified early in the program. Findings showed that synthesis of the silicon and phosphorous containing tetracarbonyl monomers would be difficult and beyond budget and schedules allowed for Task II. Thus, the objectives of Task II were modified as described below.

The modified Task II objectives are to synthesize and characterize polyphenylquinoxalines (PPQ) that have improved processibility and extended service life at elevated temperature.

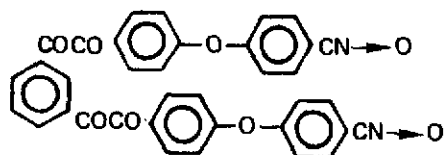
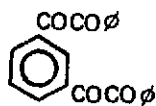
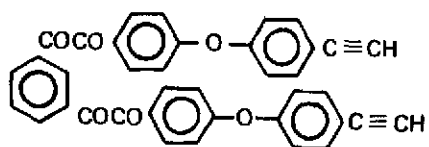
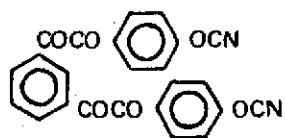
Extending polymer service life at elevated temperature was sought by decreasing the thermoplasticity of PPQs. Generally the thermoplasticity of PPQs is reduced by exposure of the polymers to excessively high temperature postcure cycles. This is believed to partly degrade the polymer thermaloxidatively. Reducing thermoplasticity of PPQ was sought by introducing latent crosslinking groups that can be made to react after formation of the linear polyphenylquinoxaline system. Incorporation of the following pendant functional groups on the backbone of PPQ molecules was sought: -OCN, -C≡CH and -CN-O. These functional groups are known to undergo the cyclization reactions shown on the following page (References 3, 4 and 5).

3.0

(Continued)



Therefore, the following tetracarbonyl compounds were selected for synthesis and subsequent reaction with tetraamines to form PPQs with potential cross-linking sites:



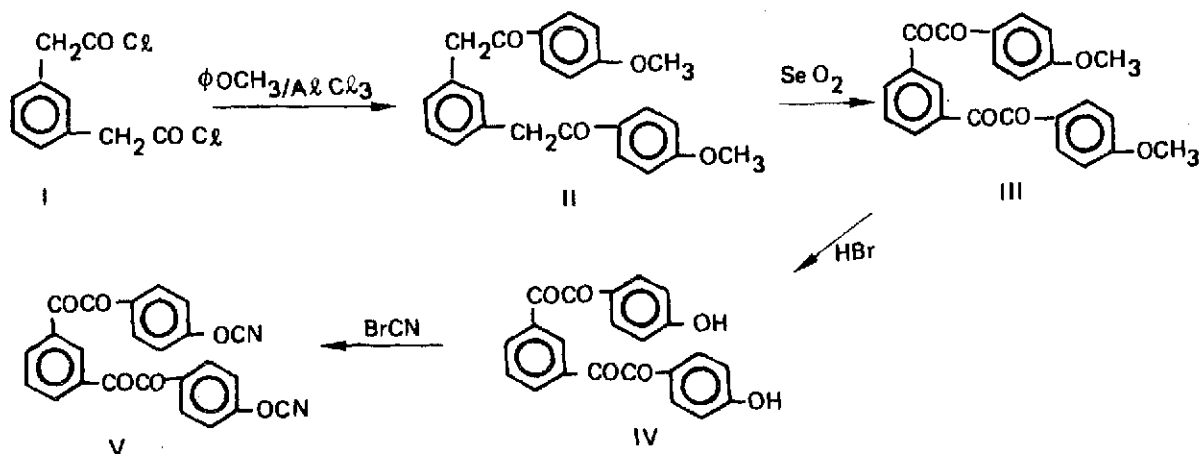
Further, improving processibility and extended service life at elevated temperature was sought through modification of a PPQ by endcapping the polymer with inert end groups. The PPQ selected for end-capping was the block copolymer (1:3) (Reference 1). This polymer has exhibited excellent processibility, and increasing its already good thermaloxidative stability was sought as a means to improve the polymer's service life at elevated temperature.

### 3.1 Synthesis and Characterization

This section on Task II work is divided into three parts. The first part describes approaches used for model compounds and reactants synthesis. The second part describes polymer synthesis approaches. The third part, in the Appendix, describes details of synthesis and characterization work.

#### 3.1.1 Reactants

Meta-bis(hydroxyphenylglyoxalyl)benzene (m-HPGB) and m-bis(p'-cyanatophenylglyoxalyl)benzene (m-CNOGB): The two tetracarbonyl compounds m-HPGB(IV) and m-CNOGB(V) were synthesized in accordance with the reaction sequence shown below.

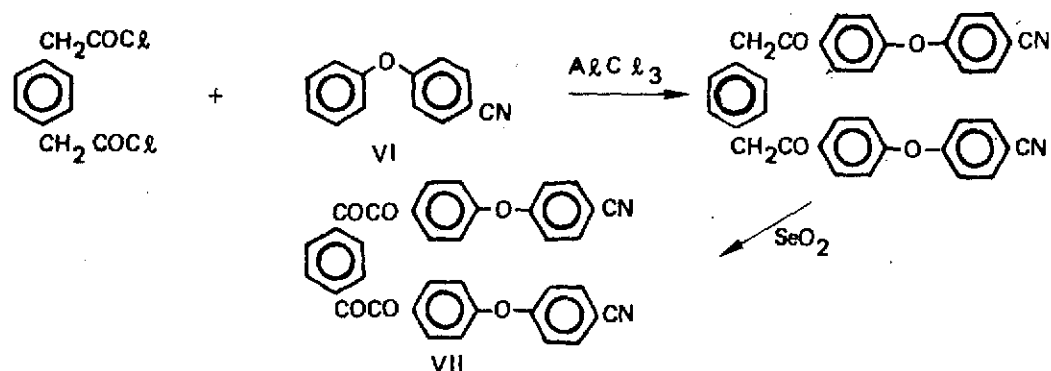


### 3.1.1 (Continued)

When placed on a preheated melting point block set at 196°C, the yellow solid m-CNOGB(V) melted at 198°C-200°C. When heated from RT, the yellow solid failed to melt up to 250°C (apparently due to trimerization of -OCN to sym-triazine). By Differential Scanning Calorimetry (DSC), at a heating rate of 60°C/min in helium, the onset of the melting endotherm occurred at 193°C with the peak at 205°C.

Para-phenoxybenzonitrile: Para-phenoxybenzonitrile(VI) was synthesized through two synthetic routes. In the first route potassium phenolate was reacted with p-bromobenzonitrile to give VI. In the second route p-phenoxyaniline was diazotized and reacted with cuprous cyanide (Reference 6 through Reference 8).

Para-bis(p'-cyanophenoxyphenylglyoxalyl)benzene (p-CPGB): The tetracarbonyl compound p-CPGB (VII) was synthesized in accordance with the reaction sequence shown below.

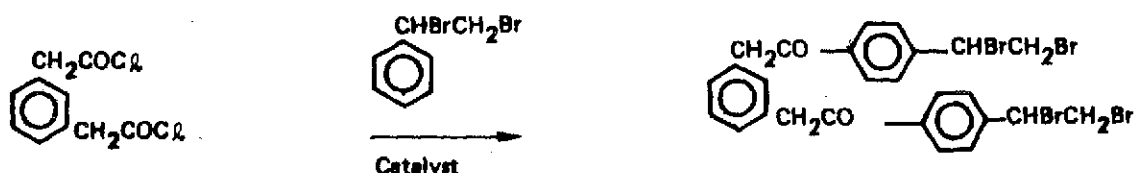


Meta-bis(p'-acetylenephenylglyoxalyl)benzene (m-ACPG): The synthesis of m-ACPG was sought using the reaction scheme shown below. The diacid chloride of m-phenylenediacetic acid was reacted with 1,2-dibromoethylbenzene and a Friedel-Crafts catalyst in an attempt to obtain the intermediate diketone. It was thought that the intermediate diketone could be oxidized

## 3.1.1

(Continued)

to the corresponding bis(1,2-dicarbonyl) compound followed by dehydrobromination to yield an acetylene bis(1,2-dicarbonyl) compound. However,

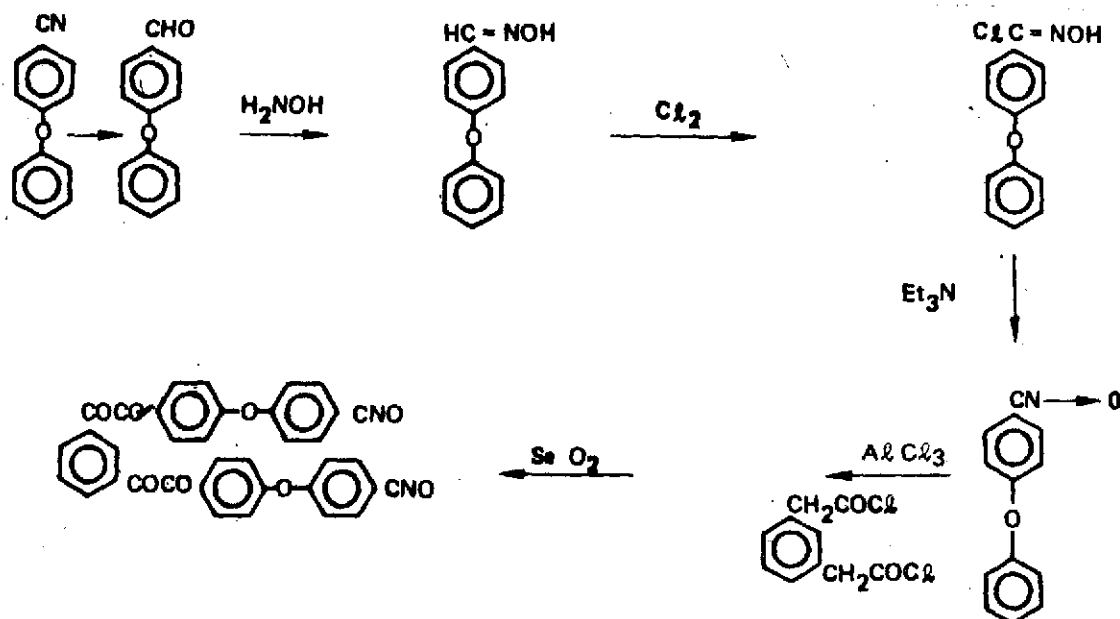


as summarized in Table 31 in the Appendix, the preparation of the intermediate diketone, to date, has been unsuccessful. Three of the four attempts resulted in a high recovery of the starting material, 1,2-dibromoethylbenzene. The other attempt (Expt. No. PH-1-263) provided an orange product, mp > 390°C, whose infrared spectrum exhibited carbonyl absorptions at 5.86μ. The insolubility as well as the high melting point suggested a polymeric material. It was thought that preferential reaction could occur between the acid chloride group and the phenyl group of 1,2-dibromoethylbenzene with the Friedel-Crafts catalyst being effectively removed by complexing with the product ketone. This would then inhibit the formation and subsequent reaction of a carbonium ion generated by the action of the catalyst on the α-bromo group. The use of a milder catalyst (stannic chloride) in place of the strong aluminum chloride failed to yield the desired product.

Para-phenoxybenzonitrile-N-oxide: The synthesis of p-phenoxybenzonitrile-N-oxide was approached from the reaction scheme shown on the following page.



3.1.1 (Continued)

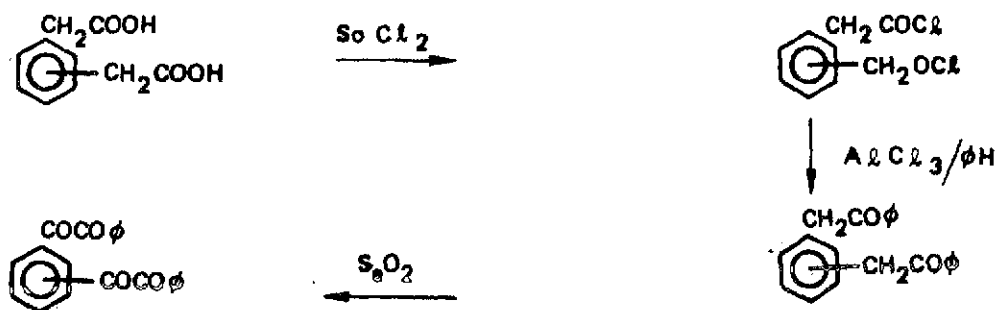


The preparation of p-phenoxybenzaldehyde from p-phenoxybenzonitrile was attempted by the Stephen reaction following a procedure given in Reference 9 for the preparation of  $\beta$ -naphthaldehyde from the corresponding nitrile. The attempted preparation of p-phenoxybenzaldehyde was sought from reaction of p-phenoxybenzonitrile with stannic chloride and hydrochloric acid. On workup, the reaction products exhibited a nitrile group absorption band in the infrared spectrum. Although there are several alternate routes for the preparation of p-phenoxybenzaldehyde, time and Task II budget did not permit pursuit of alternate synthetic approaches. Para-phenoxybenzaldehyde was sought for use in conversion to the nitrile oxide. The nitrile oxide would have been used as an intermediate in an attempt to introduce nitrile oxide groups into PPQ.

Meta-bis(phenylglyoxalyl)benzene (m-BPGB) and p-bis(phenylglyoxalyl)benzene (p-BPGB): The tetracarbonyl compounds m-BPGB (VIII) and p-BPGB (IX) (Reference 8 and Reference 10) were synthesized in accordance with the following general reaction sequence.

## 3.1.1

(Continued)



m-BPGB or p-BPGB

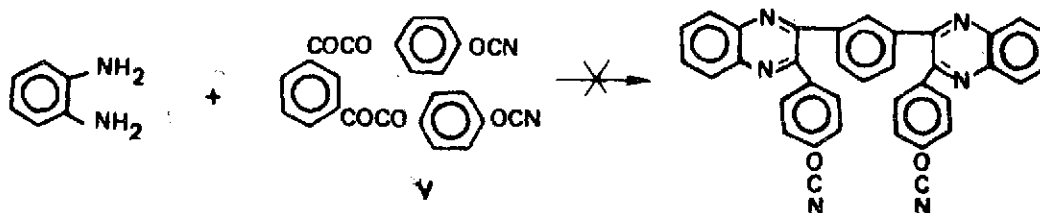
3,3'-Diaminobenzidine (DAB) and 3,3',4,4'-tetraaminobenzophenone (TAB):

The tetraamines DAB (X) and TAB (XI) were purchased from commercial sources and purified as described in the Appendix.

## 3.1.2

Model Compounds

The reaction of *o*-phenylenediamine and m-CNOGB(V) was briefly investigated.



This brief investigation was promoted because the reaction of V with 3,3'-diaminobenzidine failed to provide the desired PPQ (See Paragraph 3.1.3). A stoichiometric mixture of *o*-phenylenediamine and m-CNOGB in chloroform resulted in a system, which (after precipitation from N,N-dimethylformamide (DMF) with water and sintering at 270°C) failed to completely melt at 290°C suggesting a mixture of high melting components. One of the problems anticipated in introducing cyanato groups as latent crosslinking sites within a PPQ by this approach was the possibility of preferential reaction between the amine groups and cyanato groups rather than the desired reaction of amine and bis(1,2-dicarbonyl) groups to form the quinoxaline ring. It was originally thought that carbonyl groups para to the cyanato groups would deactivate the cyanato groups sufficiently to permit the desired reaction. Therefore, no further work with m-bis(p'-cyanatophenylglyoxalyl)benzene was planned. Cyanato groups may be introduced into PPQ

## 3.1.2

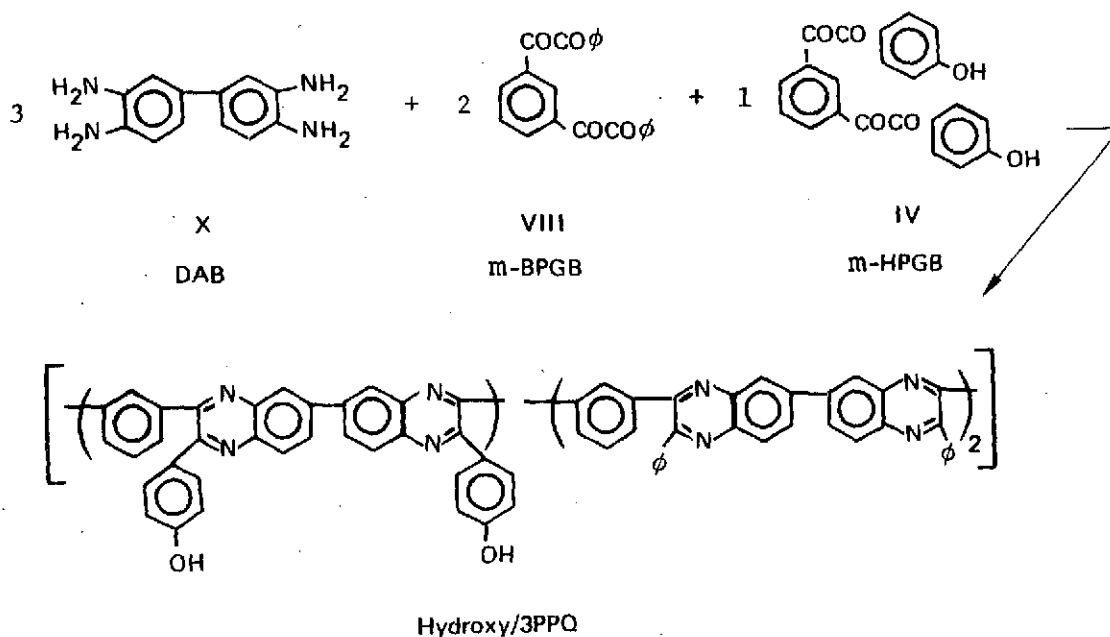
(Continued)

through an alternate approach by preparing a precursor hydroxy containing PPQ and converting the hydroxy groups into cyanato groups.

## 3.1.3

## Polymers

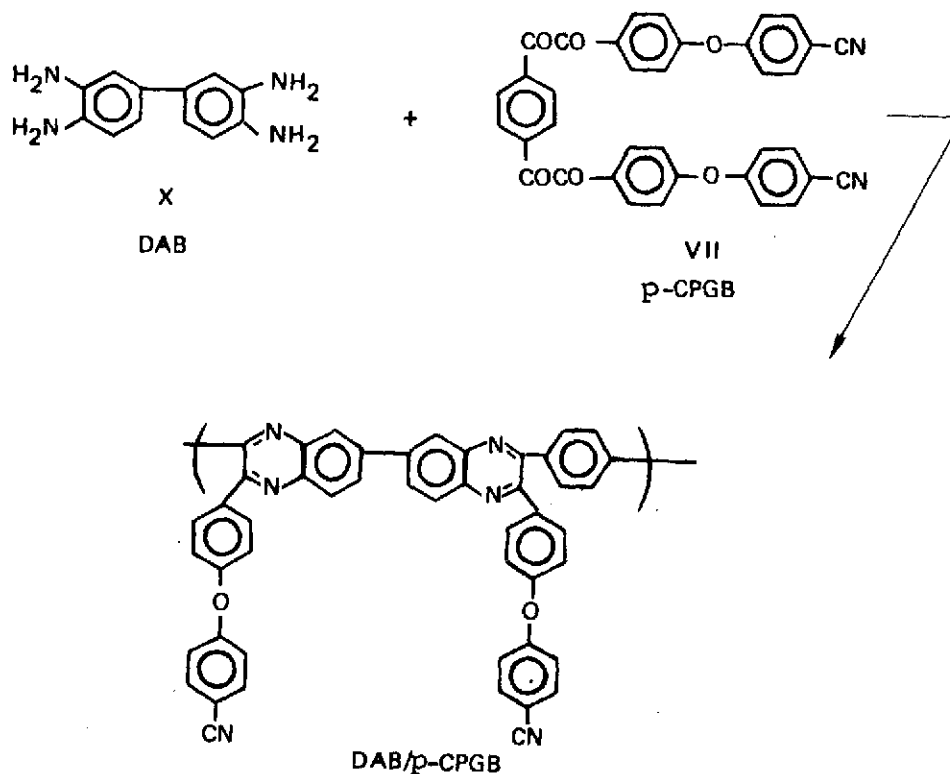
Hydroxy/3PPQ: A hydroxyl group containing PPQ (hereafter referred to as hydroxy/3PPQ) was synthesized in m-cresol from reaction of 3,3'-diaminobenzidine (DAB), m-bis(phenylglyoxalyl) benzene (m-BPGB) and m-bis(p'-hydroxyphenylglyoxalyl) benzene (m-HPGB). A ratio of DAB/m-BPGB/m-HPGB = 3/2/1 was used in the reaction.



This polymer was synthesized for use as precursor in an attempt to introduce cyanato groups as latent crosslinking site. Since cyanato groups trimerize to form symmetric triazines at relatively mild conditions

( $\sim 150^{\circ}\text{C}$ ) it was thought that a PPQ could be prepared where the number of cyanato groups were kept at low values to allow for sufficient time before the polymer became intractable during composite preparation. To enhance good dispersion of hydroxyl groups along the polymer, the hydroxyl containing monomer (m-HPGB) was added to the tetraamine (DAB) and allowed to react for a brief period. Subsequently the third tetracarbonyl compound (m-BPGB) was added to the reaction mixture. After removal from solution, the hydroxy/3PPQ failed to dissolve in chloroform, *N,N*-dimethylacetamide, *N*-methylpyrrolidone, or dimethylsulfoxide. The hydroxyl groups cannot be converted into cyanato groups with cyanogen bromide because of the polymer is insoluble in a suitable medium for the reaction.

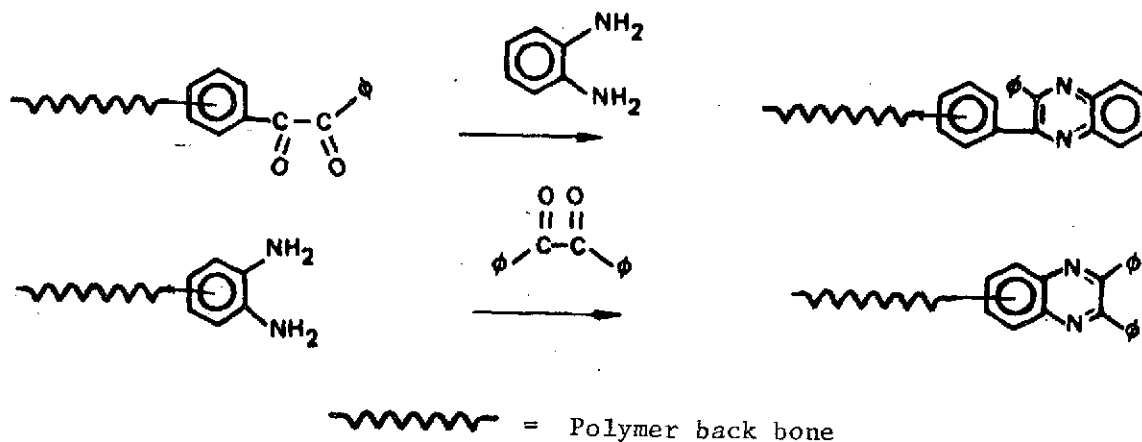
Cyano PPQ: A cyano group containing PPQ (hereafter referred to as DAB/p-CPGB) was synthesized in *m*-cresol from reaction of DAB and *p*-bis (p'-cyanophenoxyphenylglyoxalyl) benzene (p-CPGB, VII). A ratio of DAB/*m*-CPGB = 1.00 was used in the reaction.



A very viscous solution was obtained within half an hour after mixing reaction ingredients. This suggested use of more solvent for the reaction. A second synthesis was conducted using twice as much solvent as the first run. A gel was obtained after 1 hour reaction time. The gel persisted even after reducing polymer concentration to ~ 3%. A film from the diluted system was cast for isothermal aging evaluation (paragraph 3.1.4). These results suggest that a workable polymer may be achieved by upsetting the stoichiometry of the reactants.

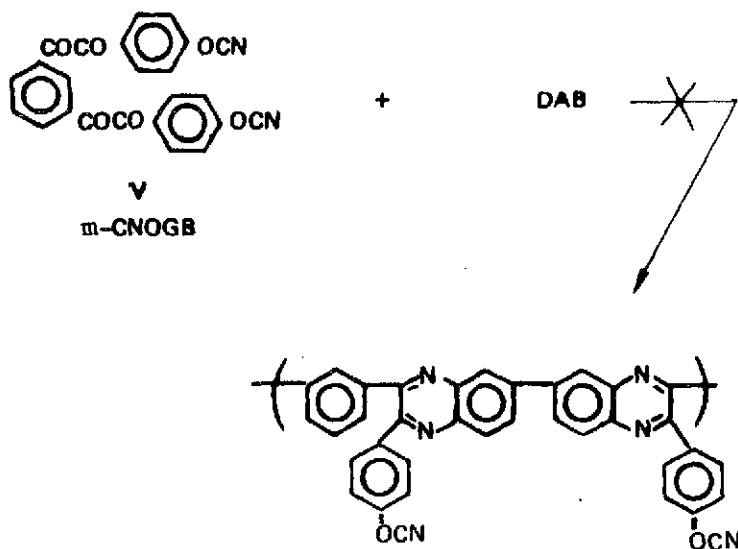
The cyano groups were introduced into the polymer for possible trimerization to symmetric triazine crosslinks in the cured polymer. A small amount of p-toluene sulfonic acid was blended thoroughly with a powdered sample of the polymer to determine if conditions conducive to CN trimerization would affect Tg of the polymer. The sample exhibited a substantial increase in Tg to 328°C. After holding at 400°C for 5 min. in N<sub>2</sub>, no Tg could be detected to 400°C. Apparently, crosslinking was occurring, presumably through trimerization to sym-triazine.

End-capped Block Copolymer (1:3): Block copolymer (1:3), first prepared under a previous contract (Reference 1), was end-capped to produce a non-functional, inert group-terminated PPQ. This was done in an effort to retain the good processibility and further extend the excellent high temperature capability of BlCo (1:3). End capping BlCo (1:3) was accomplished by reaction of the polymer with excess o-phenylenediamine. Isolation and reaction of resulting polymer with excess benzil afforded, after isolation, end-capped BlCo (1:3) as schematically shown below.



TAB/m-BPGB PPQ: A known polymer (Reference 8) (hereafter referred to as TAB/m-BPGB) was synthesized from reaction of 3,3',4,4',-tetraaminobenzophenone (TAB) and m-BPGB in a 1:1 m-cresol, xylene solution. The polymer was prepared for characterization in H-MS graphite composites in Task II and use as base for composite properties comparisons.

Cyanato PPQ: The attempted synthesis of a PPQ containing cyanato groups by reaction of m-bis(p'-cyanatophenylglyoxalyl)benzene (m-CNOGB) with DAB yielded a product having an infrared spectrum inconsistent with the desired structure.



The reaction product's infrared spectrum lacked the -OCN absorption band at 4.35 to 4.5 $\mu$ . A strong absorption band at 5.95 $\mu$  was present in the product's spectrum. The band at 5.95 $\mu$  was attributed to carbonyl groups. As discussed in the Model Compound Section of this report, (paragraph 3.1.2) one of the problems anticipated in this approach was the possibility of the amine groups reacting with the cyanato groups rather than selectively reacting with bis(1,2-dicarbonyl) groups to form desired quinoxaline rings.

The polymers described in paragraph 3.1.3 were subjected to characterization tests in terms of Brookfield viscosity, inherent viscosity ( $\eta_{inh}$ ), glass transition temperature ( $T_g$ ), and softening temperature. Results of these characterization tests are summarized in Table 1.

Four polymers were selected for further characterization in terms of thermogravimetric analyses (TGA), differential thermal analyses (DTA) and isothermal gravimetric analyses. The selected polymers were: end-capped B1Co (1:3), TAB/m-BPGB, hydroxy/3PPQ and DAB/p-CPGB. Selection of these polymers was based on their potential for ease in processing into composites. Table 10 presents the test results of simultaneous TGA and DTA of the four polymers. Table 11 and Figures 19 and 20 summarize the isothermal (316°C and 371°C) aging test results.

Excellent thermal oxidative stability at 316°C was exhibited by end-capped B1Co (1:3) and the polymer derived from TAB/m-BPGB. Although the polymer derived from DAB/p-CPGB displayed slightly lower thermal oxidative stability than end-capped B1Co (1:3) and the TAB/m-BPGB polymer, we believe that the DAB/p-CPGB polymer has at least equivalent thermal oxidative stability as the end-capped B1Co (1:3) or TAB/m-BPGB even though the results do not reflect this. The film used for isothermal aging of the TAB/p-CPGB polymer was voidy and of poor quality. Difficulty in obtaining a good film of the TAB/p-CPGB polymer was attributed to polymer gel described earlier in this report. Alternate synthetic approaches of avoiding gel formation of TAB/p-CPGB warrant further investigation. Upsetting reactant stoichiometry is one such approach. As indicated earlier, the possible poor thermal oxidative stability of hydroxy/3PPQ was anticipated.

On aging at 371°C the four polymers exhibited the same relative order of thermaloxidative stability experienced at 316°C; Namely, the end-capped B1Co (1:3) and TAB/m-BPGB polymers exhibited the highest, and

the hydroxy/3PPQ exhibited the lowest thermaloxidative stability.

The end-capped BlCo (1:3) and TAB/m-BPGB polymers were selected for further characterization in terms of Thermomechanical Analysis (TMA). Selection was based on the polymers' isothermal aging test results.

As a side investigation, polymer creep tests were conducted on the end-capped block copolymer (1:3) and TAB/m-BPGB using a 940 Thermal Mechanical Analyzer (TMA) apparatus manufactured by E. I. DuPont DeNemours and Company. The analyses were conducted to determine effects of elevated post-cure temperatures on polymer film expansion, shrinkage or flow characteristics while PPQ films are held under tensile stress at temperatures up to 450°C (842°F). Prior to the TMA tests, the end-capped BlCo (1:3) and TAB/m-BPGB films were exposed to an elevated temperature cycle of 1/2 hour at each 350°C (662°F) and 454°C (850°F). As shown in Table 12, this exposure raised the onset of polymer softening temperature and glass transition temperature of the two polymers. Control specimens were analyzed using a tension probe. Post-cured specimens were analyzed using a flat tipped penetration probe because the post-cure exposure rendered the films too brittle for cutting into "dog bone" specimens. (In a separate experiment using unpost-cured [control] film specimens of TAB/m-BPGB, it was determined that the tension probe and penetration probe yield comparable TMA traces.)

Figures 21 and 22 show superimposed TMA traces of end-capped BlCo (1:3) and TAB/m-BPGB post-cured films and controls. The results described above suggest the potential of TMA as means for determining optimum polymer cure/post-cure parameters. Studies using the TMA analyzer are recommended for future work. A suggested study approach to determine optimized cure-post-cure cycles for PPQ polymers is to correlate penetration probe loads, heat rise rates and polymer flow temperature.



TABLE 10

SIMULTANEOUS THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS  
OF POLYPHENYLQUINOXALINE POLYMERS

REACTIONS	REACTION TEMPERATURE ( $^{\circ}\text{C} \pm 5^{\circ}\text{C}$ )			
	BiCo (1:3) end-capped (PH-1-257)	TAB/m-BPGB (PH-1-247)	DAB/m-HPGB/m-BPGB (PH-1-269)	DAB/p-CPGB (PH-1-277-1)
1st Weight loss (minor)	80	85	75	75
1st Exotherm (minor)	80	100	75	75
2d Weight loss (minor)	225	--	--	
2d Exotherm (minor)	280	220	255	250
Start of major weight loss	460	515	450	505
Major weight loss	590	580	650	610
Minor weight loss	755	760	740	760
End of weight loss	860	>970	>970	>970

1

The shown reaction temperatures are the temperatures at which polymers exhibit maximum rate of weight loss or exotherm.

2

Powdered polymer samples were tested in a Mettler Simultaneous Analyzer using a nitrogen atmosphere and heat up rate of  $15^{\circ}\text{C}$  per minute.

TABLE 11  
ISOTHERMAL AGING OF POLYPHENYLQUINOXALINE POLYMER FILMS IN AIR AT 316°C AND 371°C

Polymer No.	Expt. No. PH-1-	Polymer	Weight Loss (%) <sup>5</sup>	
			400h at 316°C	200h at 371°C <sup>6</sup>
1	257	B1 Co(1:3) end capped <sup>1</sup>	4.4	33.8
2	247	TAB/m-BPGB <sup>2</sup>	7.6	34.3
3	269	DAB/m-HPGB/m-BPGB <sup>3</sup>	99.6	<sup>7</sup>
4	277-1	DAB/p-CPGB <sup>4</sup>	18.5	87

<sup>1</sup> B1Co(1:3) = block copolymer of p-bis (phenylglyoxalyl)benzene and 3,3'-diaminobenzidine polymer, p-bis(phenylglyoxalyl)benzene and 3,3', 4,4'-tetraaminobenzophenone polymer.

<sup>2</sup> m-BPGB = m-bis(phenylglyoxalyl)benzene and TAB = 3,3', 4,4'-tetraaminobenzophenone.

<sup>3</sup> DAB = 3,3'-Diaminobenzidine and m-HPGB = m-bis(p'-hydroxyphenylglyoxalyl)benzene.

<sup>4</sup> p-CPGB = p-bis(p'-cyanophenoxyphenylglyoxalyl)benzene.

<sup>5</sup> All films were aged in air circulating ovens.

<sup>6</sup> Values reflect measurements after aging films 200 hours at 371°C. Between 200 hours and 260 hours at 371°C the films' weight losses were 81% to 100% therefore these determinations were discontinued.

<sup>7</sup> Film weight loss = 100% in <100 hours at 371°F.

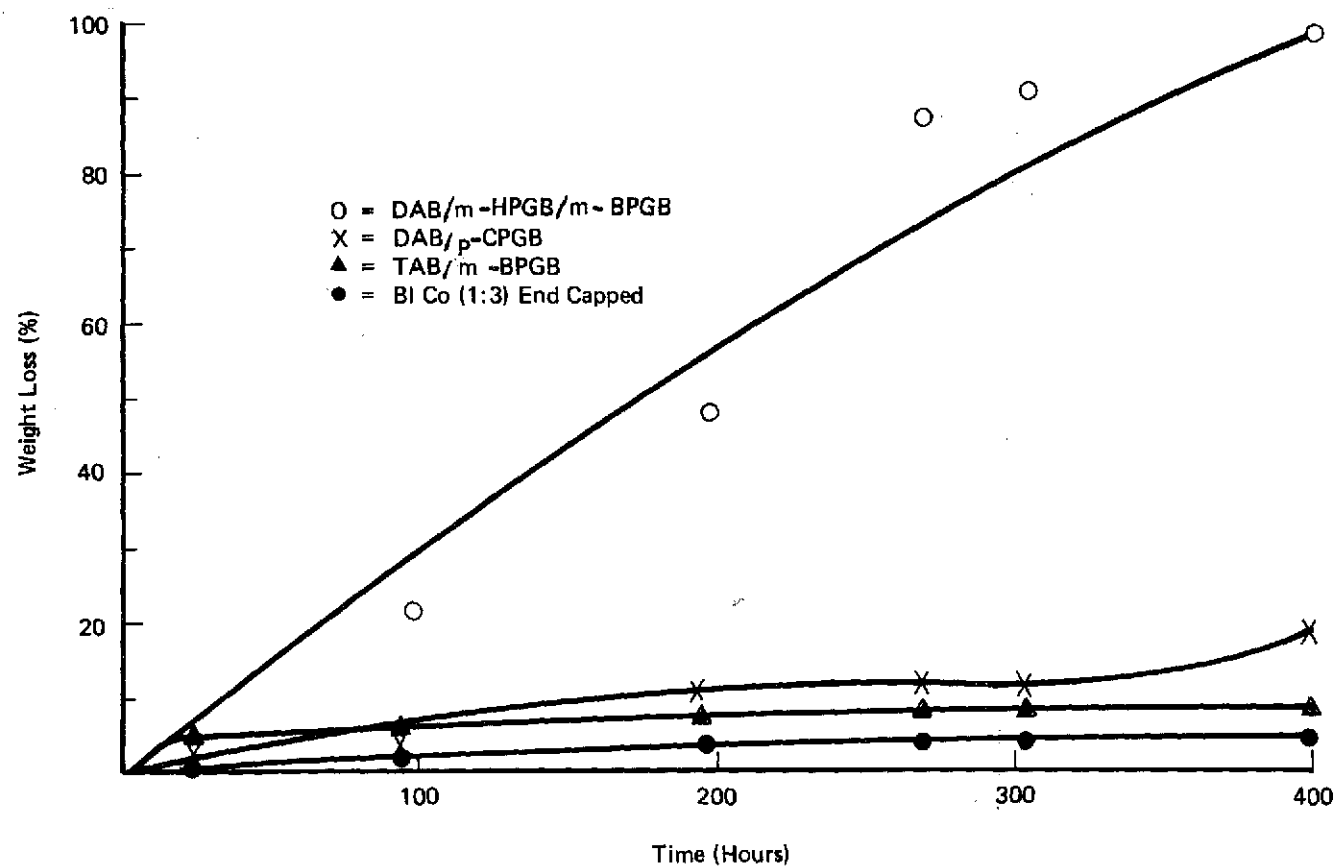


Figure 19: Isothermal (316°C) Aging of Task 2. Polymers

### 3.2

#### Polymer Selection for Task III

The end-capped BiCo (1:3) and TAB/m-BPCB were selected for cure/post cure studies in Task III. This selection was based primarily on polymer 316°C isothermal aging, TMA test results and polymer potential for ease in processibility.

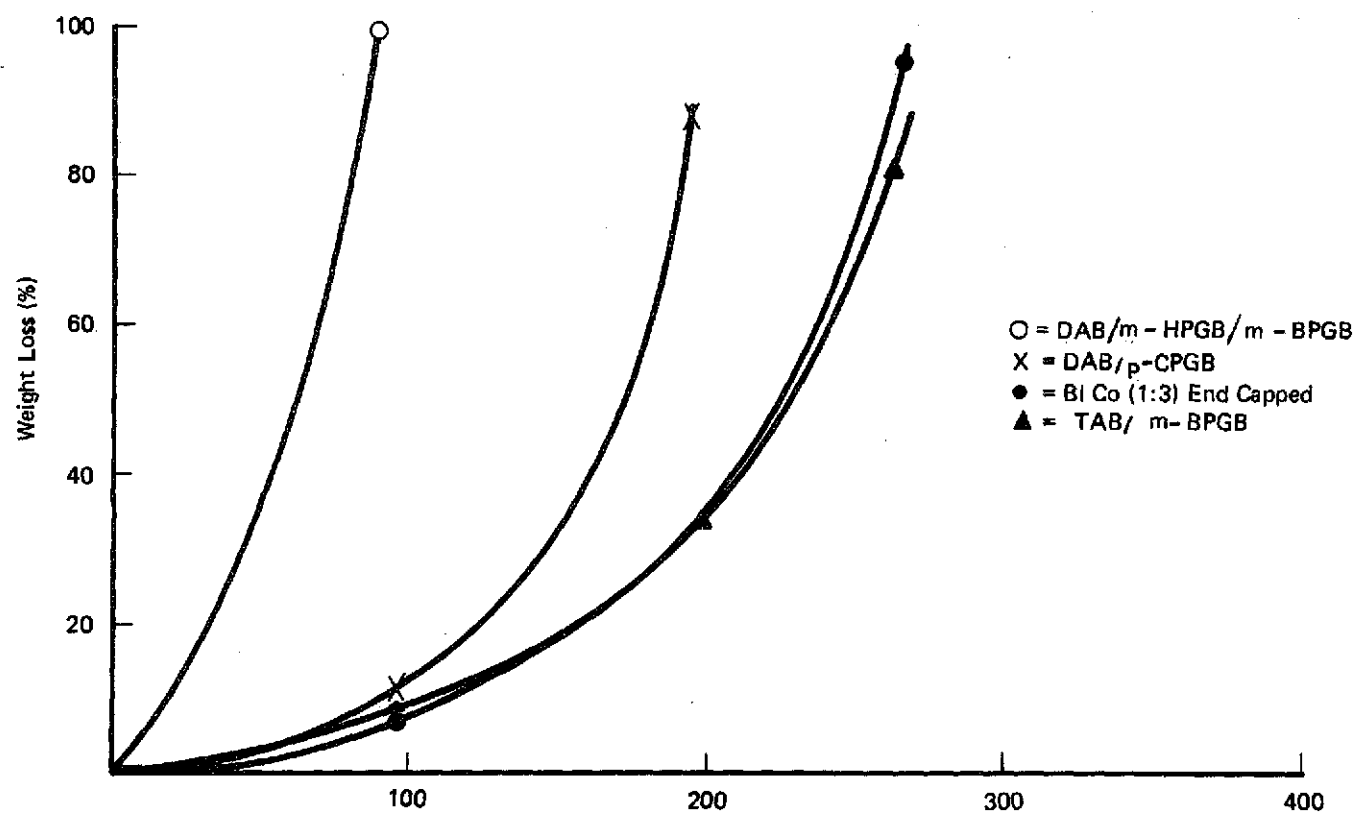


Figure 20 : Isothermal (371°C) Aging of Task 2. Polymers

TABLE 12 THERMOMECHANICAL ANALYSES OF PPQ FILMS

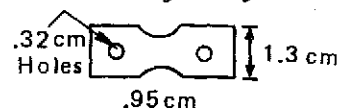
Polymer	Exp. No. PH-1-	Tg °C (DSC)	TMA Analysis Polymer Softening or Expansion Temperature			
			Control		High Temperature Exposed Specimen	
			Tg, °C	Onset of Softening Temperature (°C)	Tg, °C	Onset of Softening Temperature (°C)
B1 Co (1:3) end-capped	257	325	~300	225	~400	325
TAB/m-BPGB	247	285	~310	250	~310	285

1 E. I. duPont de Nemours and Company, 941 Thermomechanical Analyzer (TMA) was used. Heat up rate, 20°C/min.; N<sub>2</sub> atmosphere.

2 Tg determined by DSC (heat up rate, 20°C/min.; N<sub>2</sub> atmosphere).

3 Polymer films were dried at ~70°C in air (~16 hrs.) and at ~130°C in vacuo (~4 hrs.).

4 Polymer expansion was determined using a quartz tension probe loaded with 2g weight. "Dog bone" shaped specimen with the following configuration was used:



5 Polymer films were exposed to elevated temperatures of 350°C (1/2 hr.) and 454°C (1/2 hr.) prior to analyses.

6 A flat tip (0.064 sq. cm) penetration probe with a 5g load was used in place of a tension probe because the films were too brittle for cutting into "dog bone" specimens. Specimen size ~ 0.25 sq. cm.



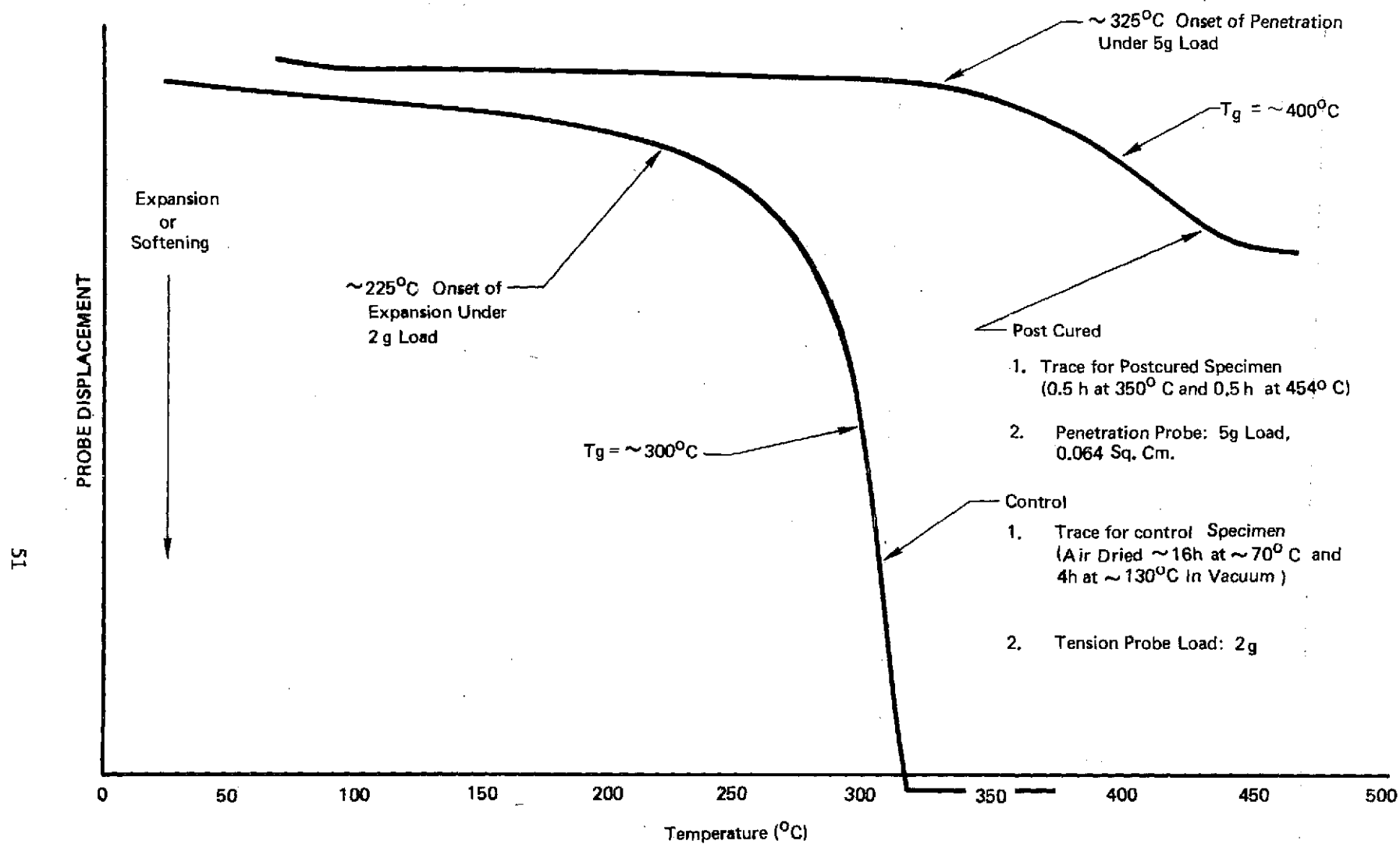


Figure 21 : Thermomechanical Analysis of End-Capped BI Co (1:3), (PH 1-257)

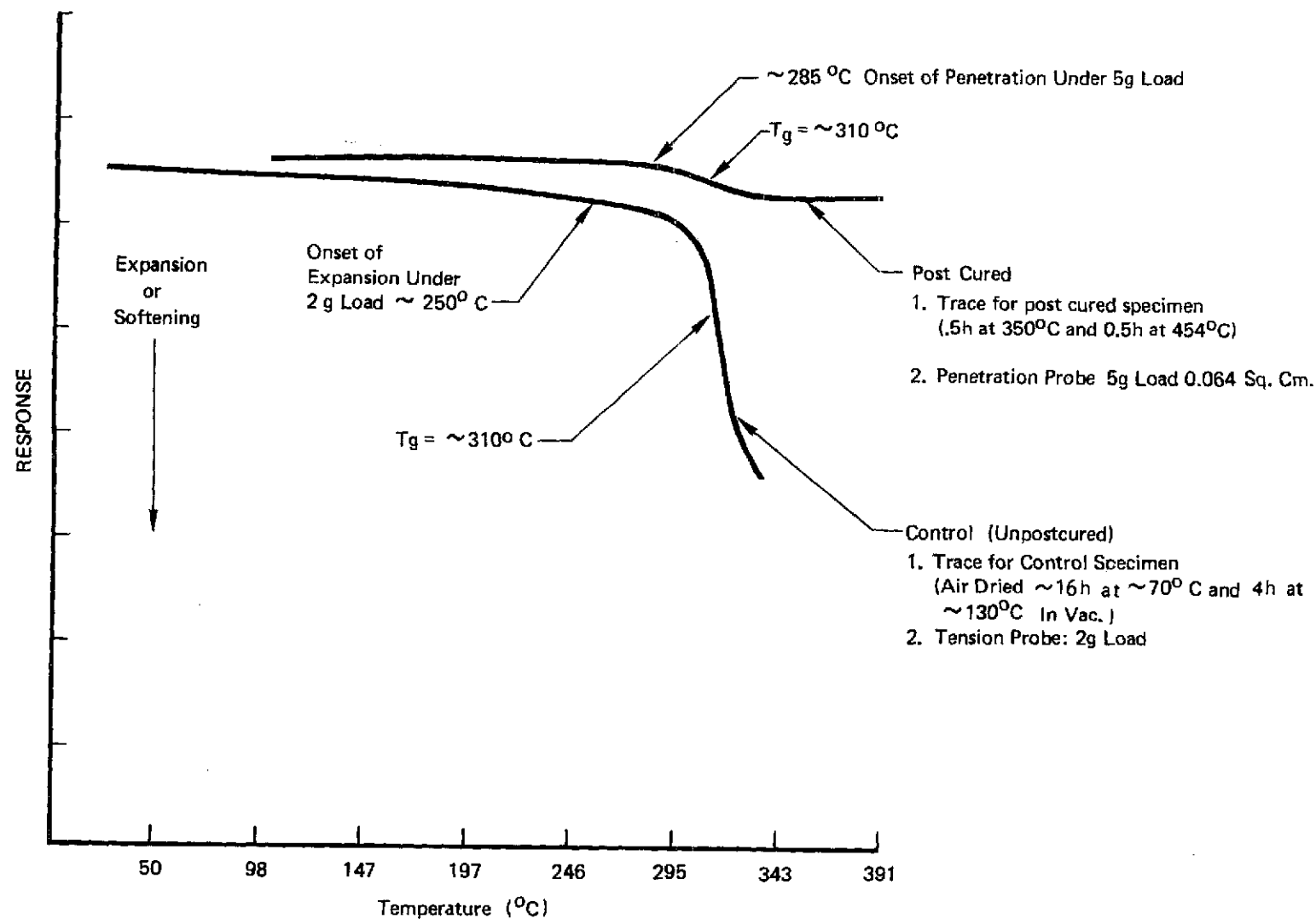


Figure: 22 Thermomechanical Analyses of TAB/m - BPGB (PH 1-247)

The end-capped block copolymer (1:3) and TAB/m-BPGB were selected from Task II for composite studies. Both polymers were synthesized using the procedures noted in Section 3.1 and characterized. Table 13 lists the Task III polymer reaction and characterization data.

Unidirectional graphite composite laminates were made with each system. The laminates, normally 0.1 inches thick, were cured one hour each at 336°C (636°F) and 454°C (850°F) under  $2.07 \times 10^6 \text{ N/m}^2$  (300 psi) and evaluated for flexural and interlaminar shear properties at +21°C (70°F), +204°C (400°F) and +316°C (600°F). The results of these tests are shown in Tables 14-17. Figures 23 and 24 show a photomicrograph of each laminate. Figures 25 and 26 show scanning electron photomicrographs of tested flexural specimens from each laminate.

The laminates were subjected to 316°C (600°F) isothermal aging and these results are shown in Table 18.

TABLE 13 CHARACTERIZATION OF TASK III POLYMERS

Polymer No.	Exp't No. PH-1-	Polymer	Stoichiometry <sup>1</sup> NH <sub>2</sub> /CO	R <sub>x</sub> Scale, Mole	Conc <sup>2</sup> , % Solids	Solvent	Sol'n <sup>3</sup> Vis. cps	$\eta_{inh}$ <sup>4</sup> dl/g
1	247 JS11	TAB/m-BPGB <sup>5</sup>	0.995/1.00	0.15	18%	m-cresol xylene (1:1)	2430	1.05
2	246 JS11	B1 Co (1:3)	0.985/1.00	0.24	16%	↓	--	1.87
3	257 JS12	B1 Co (1:3) end-capped	Polymer #2	--	16%	↓	---	1.53

- <sup>1</sup> Mole ratio of tetraamine to tetracarbonyl monomer
- <sup>2</sup> Based upon the weight of polymer and volume of solvent
- <sup>3</sup> Brookfield viscosity at 25°C
- <sup>4</sup> Inherent viscosity in 0.5% m-cresol solution at 25°C
- <sup>5</sup> TAB = 3,3',4,4'-tetraaminobenzophenone and m-BPGB = m-bis(phenylglyoxalyl)benzene

TABLE 14 PROPERTIES OF TAB/m-BPGb GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE °C (°F)	FLEXURAL PROPERTIES				INTERLAMINAR SHEAR STRENGTH	
	TIME HRS.	TEMPERATURE °C (°F)		STRENGTH 10 <sup>8</sup> N/m <sup>2</sup> (10 <sup>3</sup> psi)		MODULUS 10 <sup>10</sup> N/m <sup>2</sup> (10 <sup>6</sup> psi)		10 <sup>6</sup> N/m <sup>2</sup> (psi)	
36 * ↓	—	21 (70)	21 (70)	7.83	(113.6)	11.7	(17.0)	39.7	(5760)
				9.17	(133.0)	12.3	(17.8)	41.0	(5940)
				<u>7.87</u>	<u>(114.1)</u>	<u>12.0</u>	<u>(17.4)</u>	<u>40.4</u>	<u>(5860)</u>
				8.29	(120.2)	12.0	(17.4)	40.3	(5850)
	.1	204 (400)	204 (400)	7.70	(111.6)	14.8	(21.4)	40.6	(5880)
				7.86	(113.9)	13.9	(20.1)	37.2	(5390)
				<u>8.19</u>	<u>(118.7)</u>	<u>14.3</u>	<u>(20.8)</u>	<u>39.3</u>	<u>(5700)</u>
				7.91	(114.7)	14.3	(20.8)	39.0	(5660)
	.1	316 (600)	316 (600)	1.39	(20.2)	1.6	(2.3)	11.8	(1710)
				1.74	(25.3)	3.5	(5.1)	11.0	(1600)
				<u>1.94</u>	<u>(28.2)</u>	<u>4.3</u>	<u>(6.2)</u>	<u>14.3</u>	<u>(2070)</u>
				1.69	(24.6)	3.1	(4.5)	12.4	(1790)

\* Polymer batch PH-1-247 JS-11

Laminate cure: 1 hr at each 336°C(636°F) and  
455°C(850°F) and 2.07 x 10<sup>6</sup> N/m<sup>2</sup>(300 psi)

Fiber Volume: 61%

TABLE 15 PROPERTIES OF TAB/m-BPGB GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE		FLEXURAL PROPERTIES	
	TIME HRS.	TEMPERATURE °C (°F)	°C	(°F)	STRENGTH 10 <sup>8</sup> N/m <sup>2</sup> (10 <sup>3</sup> psi)	MODULUS 10 <sup>10</sup> N/m <sup>2</sup> (10 <sup>6</sup> psi)
36*	1	316 (600)	316	(600)	1.39 (20.2)	1.6 (2.3)
					1.74 (25.3)	3.5 (5.1)
					<u>1.94</u> (28.2)	<u>4.3</u> (6.2)
					1.69 (24.6)	3.1 (4.5)
	100				2.88 (41.7)	5.1 (7.4)
					4.23 (61.3)	9.4 (13.6)
					<u>3.63</u> (52.6)	<u>7.4</u> (10.7)
					3.58 (51.9)	7.3 (10.6)
	200				3.61 (52.4)	9.6 (13.9)
					4.41 (64.0)	9.5 (13.8)
					<u>2.80</u> (40.6)	<u>6.3</u> (9.2)
					3.61 (52.3)	8.5 (12.3)
	400				3.06 (44.4)	6.3 (9.2)
					3.61 (52.3)	9.2 (13.4)
					<u>3.32</u> (48.2)	<u>7.4</u> (10.7)
					3.33 (48.3)	7.6 (11.1)
	500				3.54 (51.4)	7.6 (11.0)
					2.68 (38.9)	6.1 (8.8)
					<u>3.12</u> (45.3)	<u>7.4</u> (10.8)
					3.11 (45.2)	7.0 (10.2)

\* Polymer batch PH-1-247 JS-11

Laminate cure: 1 hr at each 336°C(636°F) and  
455°C(850°F) and 2.07 x 10<sup>6</sup>N/m<sup>2</sup>(300 psi)

Fiber Volume: 61%



TABLE 16 PROPERTIES OF END CAPPED B1Co (1:3) GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE °C (°F)	FLEXURAL PROPERTIES				Interlaminar Shear Strength 10 <sup>6</sup> N/m <sup>2</sup> (psi)								
	TIME HRS.	TEMPERATURE °C (°F)		STRENGTH 10 <sup>8</sup> N/m <sup>2</sup> (10 <sup>3</sup> psi)		MODULUS 10 <sup>10</sup> N/m <sup>2</sup> (10 <sup>6</sup> psi)										
37* ↓		21 (70)	21 (70)	5.83 (84.5)	6.94 (100.7)	7.41 (107.4)	6.72 (97.5)	14.2 (20.6)	13.2 (19.1)	15.2 (22.1)	14.2 (20.6)	36.7 (5320)	33.1 (4800)	34.0 (4930)	34.6 (5020)	
	.1	204 (400)	204 (400)	6.34 (92.0)	5.75 (83.4)	6.76 (98.0)	6.28 (91.1)	12.1 (17.5)	12.6 (18.2)	13.3 (19.3)	12.6 (18.3)	25.2 (3660)	28.5 (4130)	32.9 (4770)	28.9 (4190)	
	.1	316 (600)	316 (600)	3.82 (55.4)	3.11 (45.1)	3.88 (56.2)	3.60 (52.2)	9.9 (14.3)	8.7 (12.6)	9.9 (14.4)	9.5 (13.8)	20.7 (3000)	22.6 (3280)	19.1 (2770)	20.8 (3020)	

\* Polymer batch PH-1-257 JS-12

Laminate cure: 1 hr at each 336°C(636°F) and  
445°C(850°F) and 2.07 x 10<sup>6</sup> N/m<sup>2</sup> (300 psi)

Fiber Volume: 63%

TABLE 17 PROPERTIES OF ENDCAPPED B<sub>2</sub>Co(1:3) GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE °C (°F)		FLEXURAL PROPERTIES			
	TIME HRS.	TEMPERATURE °C (°F)			STRENGTH 10 <sup>8</sup> N/m <sup>2</sup> (10 <sup>3</sup> psi)		MODULUS 10 <sup>10</sup> N/m <sup>2</sup> (10 <sup>6</sup> psi)	
37* ↓	.1	316 (600)	316 (600)	3.82	(55.4)	9.9	(14.3)	
				3.11	(45.1)	8.7	(12.6)	
				3.87	(56.3)	9.9	(14.4)	
				3.60	(52.3)	9.5	(13.8)	
	100			4.59	(66.6)	9.9	(14.3)	
				4.69	(68.0)	10.3	(14.9)	
				4.68	(67.8)	10.1	(14.6)	
				4.65	(67.5)	10.1	(14.6)	
	200			3.61	(52.4)	9.6	(13.9)	
				4.41	(64.0)	9.5	(13.8)	
				2.80	(40.6)	6.3	( 9.2)	
				3.61	(52.3)	8.5	(12.3)	
	400			3.35	(48.6)	6.8	(9.8)	
				3.32	(48.1)	6.6	(9.6)	
				2.83	(41.1)	6.3	(9.1)	
				3.17	(45.9)	6.6	(9.5)	
	500			3.08	(44.7)	5.4	(7.9)	
				2.66	(38.5)	4.6	(6.7)	
				2.86	(41.5)	5.1	(7.4)	
				2.87	(41.6)	5.0	(7.3)	

\* Polymer batch PH-1-257 JS-12

Laminate cure: 1 hr at 336°C(636°F) and  
445°C(850°F) and 2.07 x 10<sup>6</sup> N/m<sup>2</sup>(300 psi)

Fiber Volume: 63%





Figure 23: Cross Section of Laminate No. 37 (X65)



Figure 24: Cross Section of Laminate No. 36 (X65)

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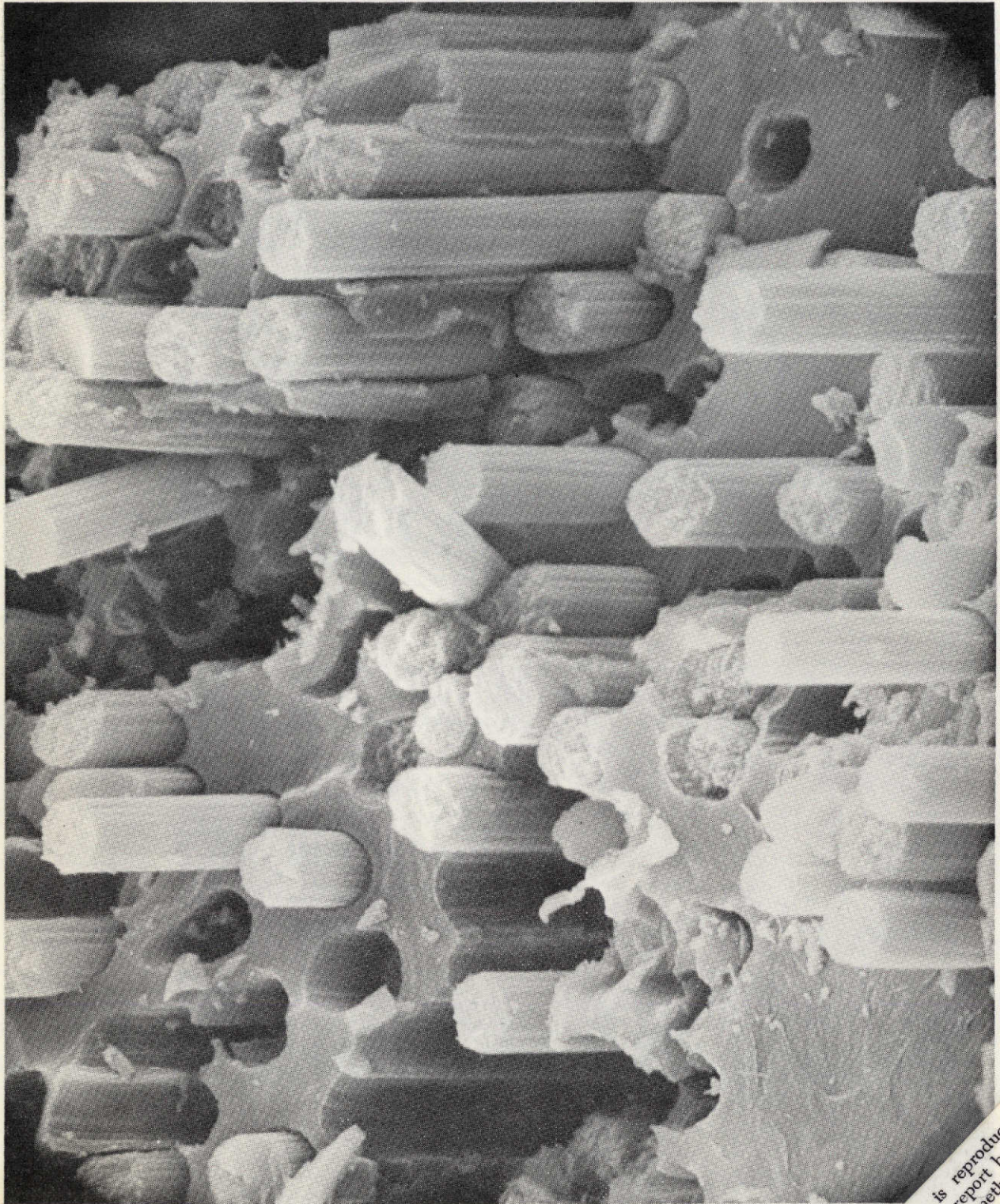


Figure 25: Electron Photomicrograph of Flexural Test Failure Area  
Laminate No. 37 (X600)

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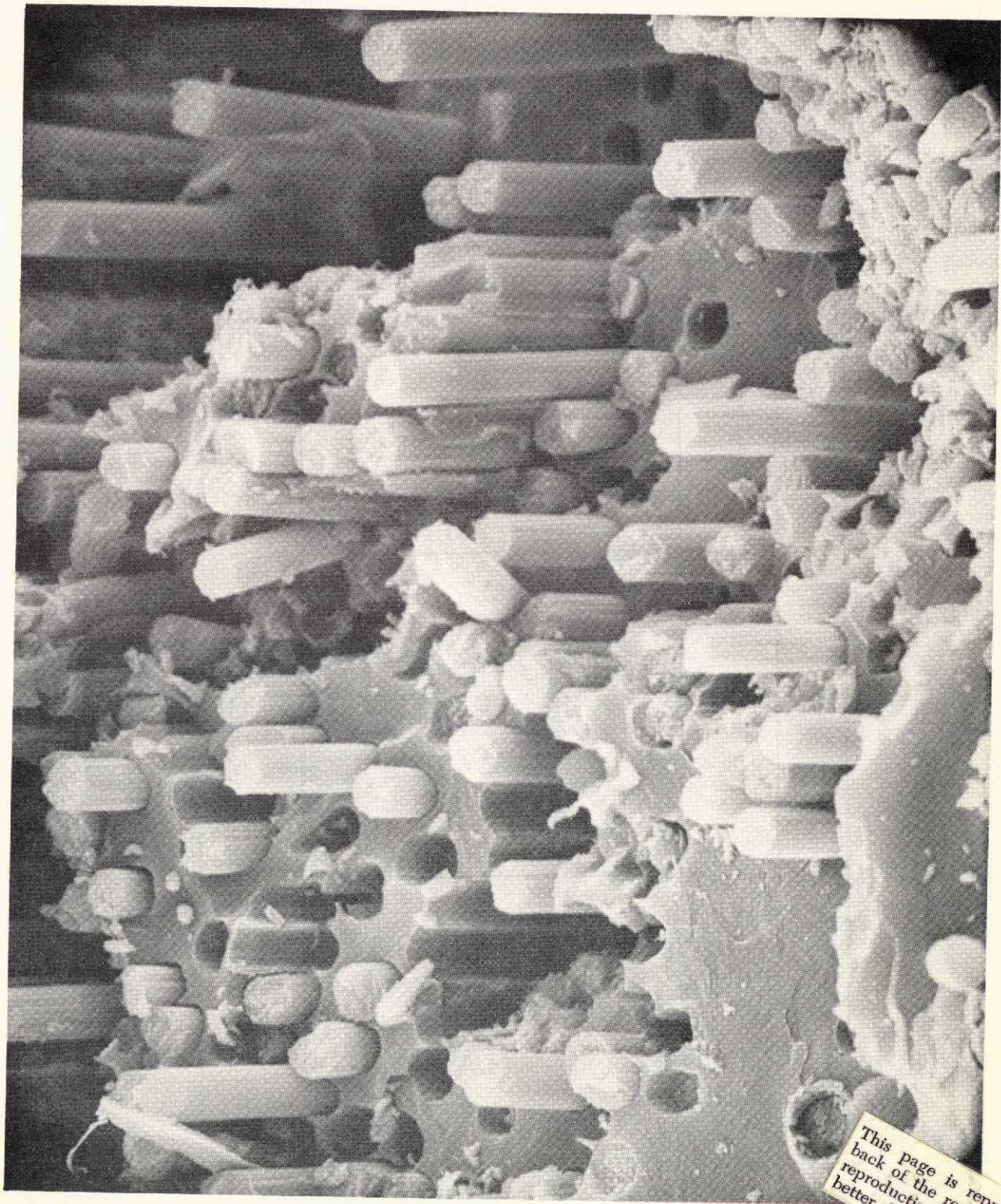


Figure 26: Electron Photomicrograph on Flexural Test Failure Area  
Laminate No. 36 (X600)

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Table 18 ISOTHERMAL AGING OF B1Co (1:3) END-CAPPED AND  
TAB/m-BPGB GRAPHITE COMPOSITES AT 316°C (600°F)

HOURS AGING (316°C)	WEIGHT LOSS (%)	
	B1Co (1:3) END-CAPPED	TAB/m-BPGB
100	2.30	1.10
200	3.15	1.60
300	4.10	2.94
400	5.40	5.70
500	6.80	6.50



The objective of this task was to perform more extensive properties studies on the best polymer from Task I and III. However, a review of the Task I and Task III composite results indicated that the random copolymer (1:3) via PMR, PPQ-II via PMR, end-capped B1Co- (1:3), and the TAB/m-BPGB were relatively comparable in mechanical and thermal properties. One composite would demonstrate slightly better mechanical properties but then show less thermal stability or vice versa. The net result was that an arbitrary selection had to be made as to the two composites which would be evaluated in this task. Since the random copolymer (1:3) and PPQ-II were studied under a previous program [Reference 1; although using different processing parameters], it was decided to evaluate the end-capped B1Co (1:3) and the TAB/m-BPGB in more depth. Each of these polymers were synthesized using the procedures stated in Task II and characterized. Results of the polymer characterizations are tabulated in Table 19.

Graphite (HM-S) composite laminates were fabricated using established procedures and a cure cycle of one hour each at 336°C (636°F) and 399°C (850°F) under  $2.07 \times 10^6$  N/m<sup>2</sup> (300 psi). The following property determinations were conducted at +21°C (70°F), +204°C (400°F) and +316°C (600°F):

- Tensile strength and modulus
- Compressive strength
- Flexural strength and modulus
- Interlaminar shear strength

The results of these tests are shown in Tables 20 to 25. A Poissons ratio of 0.33 and 0.37 were obtained for the end-capped B1Co (1:3) and the TAB/m-BPGB polymers respectively.

Notched-izod impact tests were conducted and these results are shown in Figure 27.

The thermal stability of the composites is illustrated in Tables 26-30. Figures 28 and 29 show a photomicrograph of each laminate. Figures 30 and 31 show scanning electron photomicrographs of tested flexural specimens from each laminate.

TABLE 19 CHARACTERIZATION OF TASK IV POLYMERS

POLYMER	EXPERIMENT NO. PH-1-	REACTION SCALE (MOLE)	CONCENTRATION (% SOLIDS)	INHERENT VISCOSITY dl/g*
TAB/m-BPGB	247-JS13	.79	18	1.05
B1Co (1:3) end-capped	257-JS16	.41	16	1.79
B1Co (1:3) end-capped	257-JS17	.41	16	1.10

\* 0.5% solution in m-cresol at 25°C

TABLE 20 PROPERTIES OF END-CAPPED B1Co (1:3) GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE °C (°F)	FLEXURAL PROPERTIES				INTERLAMINAR SHEAR	
	TIME (HRS.)	TEMPERATURE °C (°F)		STRENGTH $10^8 \text{ N/m}^2$ ( $10^3 \text{ psi}$ )		MODULUS $10^{10} \text{ N/m}^2$ ( $10^6 \text{ psi}$ )		$10^6 \text{ N/m}^2$ STRENGTH (psi)	
38*	-	21 (70)	21 (70)	5.33	(77.3)	12.9	(18.7)	27.9	(4040)
				8.56	(124.1)	10.8	(15.6)	28.8	(4170)
				7.00	(101.5)	11.8	(17.1)	28.1	(4070)
				6.96	(101.0)	11.8	(17.1)	28.2	(4090)
	.1	204 (400)	204 (400)	6.94	(100.6)	11.6	(16.8)	27.8	(4030)
				6.00	( 87.0)	11.5	(16.7)	26.7	(3870)
				7.46	(108.2)	12.8	(18.5)	26.6	(3850)
				6.80	( 98.6)	12.0	(17.3)	27.0	(3920)
	.1	316 (600)	316 (600)	3.18	( 46.1)	6.3	( 9.1)	24.2	(3510)
				3.99	( 57.9)	8.9	(12.9)	25.0	(3620)
				2.66	( 38.5)	7.5	(10.9)	23.4	(3390)
				3.28	(47.5)	7.6	(11.0)	24.2	(3510)

\* Polymer batch PH-1-257 JS16

Laminate cure: 1 hr at each  $336^\circ\text{C}$  ( $636^\circ\text{F}$ ) and  
 $455^\circ\text{C}$  ( $850^\circ\text{F}$ ) and  $2.07 \times 10^6 \text{ N/m}^2$  (300 psi)

Fiber Volume: 61% by weight



TABLE 21 TENSILE PROPERTIES OF END-CAPPED B1Co (1:3) GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE		TENSILE PROPERTIES			
	TIME (Hrs.)	TEMPERATURE °C (°F)	°C (°F)	°C (°F)	STRENGTH 10 <sup>8</sup> N/m <sup>2</sup> (10 <sup>3</sup> psi)		MODULUS 10 <sup>10</sup> N/m <sup>2</sup> (10 <sup>6</sup> psi)	
38b *	--	21 (70)	21 (70)		9.02	(130.8)	17.7	(25.6)
					9.57	(138.8)	17.4	(25.2)
					11.13	(161.4)	21.5	(31.2)
					9.91	(143.7)	18.9	(27.3)
	.1	204 (400)	204 (400)		9.41	(136.4)	18.3	(26.5)
					9.19	(133.3)	21.0	(30.5)
					7.82	(113.4)	16.5	(23.9)
					8.81	(127.7)	18.6	(27.0)
	.1	316 (600)	316 (600)		6.87	(99.6)	13.9	(20.2)
					6.84	(99.2)	18.5	(26.8)
					8.44	(122.4)	15.0	(21.8)
					7.38	(107.1)	15.8	(22.9)

\* Polymer batch PH-1-257 JS17  
 Laminate cure: 1 hr at each 336°C(636°F) and  
 455°C(850°F) and 2.07 x 10<sup>6</sup> N/m<sup>2</sup> (300 psi)  
 Fiber Volume: 61% weight

TABLE 22 COMPRESSION PROPERTIES OF END-CAPPED B1Co (1:3) GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE		COMPRESSION PROPERTIES			
	TIME (Hrs.)	TEMPERATURE °C (°F)			STRENGTH		MODULUS	
					10 <sup>8</sup> N/m <sup>2</sup>	(10 <sup>3</sup> psi)	10 <sup>10</sup> N/m <sup>2</sup>	(10 <sup>6</sup> psi)
38b*	--	21 (70)	21 (70)		8.59	(124.5)	18.1	(26.3)
					9.08	(131.6)	16.8	(24.4)
					8.73	(126.6)	17.4	(25.2)
					8.80	(127.6)	17.4	(25.3)
	.1	204 (400)	204 (400)		8.88	(128.8)	14.5	(21.0)
					9.16	(132.8)	13.9	(20.2)
					8.80	(127.6)	13.8	(20.0)
					8.94	(129.7)	14.1	(20.4)
	.1	316 (600)	316 (600)		3.59	(52.1)	8.4	(12.2)
					5.85	(84.8)	11.4	(16.5)
					4.61	(66.8)	10.5	(15.2)
					4.68	(67.9)	10.1	(14.6)

\* Polymer batch PH-1-257 JS17

Laminate cure: 1 hr at each 336°C(636°F) and  
455°C(850°F) and  $2.07 \times 10^6$  N/m<sup>2</sup> (300 psi)

Fiber Volume: 61% by weight

TABLE 23 PROPERTIES OF TAB/m-BPGb GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE °C      (°F)	FLEXURAL PROPERTIES				INTERLAMINAR SHEAR STRENGTH 10 <sup>6</sup> N/m <sup>2</sup> (psi)	
	TIME (HRS.)	TEMPERATURE °C    (°F)		STRENGTH		MODULUS			
				10 <sup>8</sup> N/m <sup>2</sup>	(10 <sup>3</sup> psi)	10 <sup>10</sup> N/m <sup>2</sup>	(10 <sup>6</sup> psi)		
39 * ↓	-	21    (70)	21      (70)	9.52	(138.0)	14.1	(20.5)	29.1	(4220)
				9.88	(143.3)	14.7	(21.3)	28.2	(4090)
				9.43	(136.7)	13.7	(19.9)	28.8	(4170)
				9.61	(139.3)	14.2	(20.6)	28.7	(4160)
	.1	204   (400)	204      (400)	6.90	(100.0)	12.6	(18.2)	34.3	(4980)
				7.84	(113.7)	14.8	(21.5)	32.3	(4690)
				7.94	(115.2)	13.3	(19.3)	28.9	(4190)
				7.56	(109.6)	13.6	(19.7)	31.8	(4620)
↓	.1	316   (600)	316      (600)	4.23	( 61.4)	9.2	(13.3)	27.8	(4030)
				2.87	( 41.6)	6.1	( 8.8)	28.2	(4090)
				4.92	( 71.3)	11.0	(16.0)	23.4	(3390)
				4.01	( 58.1)	8.8	(12.7)	26.5	(3840)

\* Polymer batch PH-1-247 JS13  
 Laminate cure: 1 hr at each 336°C (636°F) and  
 455°C (850°F) and  $2.07 \times 10^6$  N/m<sup>2</sup> (300 psi)  
 Fiber Volume: 60% weight

TABLE 24 TENSILE PROPERTIES OF TAB/m-BPGB GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE		TENSILE PROPERTIES			
	TIME (Hrs.)	TEMPERATURE °C (°F)	°C (°F)	°C (°F)	STRENGTH 10 <sup>8</sup> N/m <sup>2</sup> (10 <sup>3</sup> psi)		MODULUS 10 <sup>10</sup> N/m <sup>2</sup> (10 <sup>6</sup> psi)	
39*	--	21 (70)	21 (70)		11.62	(168.5)	16.7	(24.2)
					9.84	(142.7)	16.1	(23.3)
					9.41	(136.5)	16.0	(23.2)
					10.29	(149.2)	16.3	(23.6)
	.1	204 (400)	204 (400)		8.47	(122.8)	14.2	(20.6)
					6.87	(99.6)	14.8	(21.4)
					7.04	(102.1)	16.4	(23.8)
					7.46	(108.2)	15.1	(21.9)
	.1	316 (600)	316 (400)		9.95	(144.3)	16.6	(24.1)
					9.35	(135.6)	16.2	(23.5)
					7.92	(114.9)	15.4	(22.3)
					9.07	(131.6)	16.1	(23.3)

\* Polymer batch PH-1-247 JS13  
 Laminate cure: 1 hr at each 336°C (636°F) and  
 455°C (850°F) and  $2.07 \times 10^6$  N/m<sup>2</sup> (300 psi)  
 Fiber Volume: 60% weight



TABLE 25 COMPRESSION PROPERTIES OF TAB/m-BPGB GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE		COMPRESSION PROPERTIES			
	TIME (Hrs.)	TEMPERATURE °C (°F)			STRENGTH		MODULUS	
					$10^8 \text{ N/m}^2$	$(10^3 \text{ psi})$	$10^{10} \text{ N/m}^2$	$(10^6 \text{ psi})$
39 *	—	21 (70)	21 70		6.66	(96.5)	12.1	(17.5)
					7.18	(104.1)	12.3	(17.9)
					6.80	(98.6)	12.1	(17.6)
					6.88	(99.7)	12.2	(17.7)
	.1	204 (400)	204 (400)		6.72	(97.5)	11.9	(17.3)
					9.71	(140.8)	12.3	(17.8)
					7.57	(109.8)	12.1	(17.6)
					8.00	(116.0)	12.1	(17.6)
	.1	316 (600)	316 (600)		2.63**	(38.1)	9.7	(14.0)
					3.24	(47.0)	11.9	(17.2)
					3.86	(55.9)	12.3	(17.8)
					3.24	(47.0)	11.3	(16.3)

\* Polymer batch PH-1-247 JS13  
 Laminate cure: 1 hr at each 336°C (636°F) and  
 455°C (850°F) and  $2.07 \times 10^6 \text{ N/m}^2$  (300 psi)  
 Fiber Volume: 60% weight

\*\* All three specimens had end failure

Figure 27 IZOD Impact Strength\* PPQ/Graphite Laminates

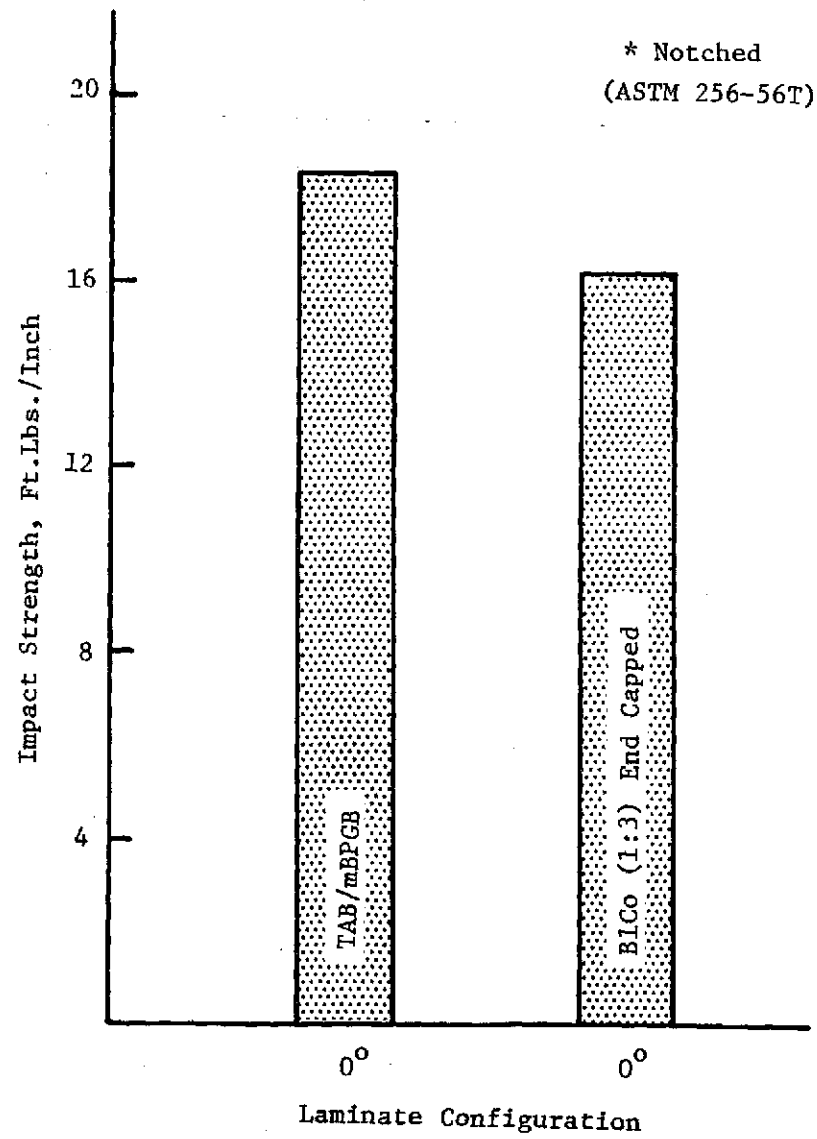


Table 26 ISOTHERMAL AGING OF B1Co (1:3) END-CAPPED AND TAB/m-BPGB  
GRAPHITE COMPOSITES AT 204°C (400°F) AND 316°C (600°F)

HOURS AGING	WEIGHT LOSS (%)			
	B1Co (1:3) END-CAPPED AGING TEMPERATURE (°C)		TAB/m-BPGB AGING TEMPERATURE (°C)	
	204	316	204	316
10	.03	1.70	.03	.82
100	.085	3.20	.06	1.80
300	.086	3.90	.12	2.80
600	.126	6.30	.124	6.20
1000	.12	12.70	.12	13.6

TABLE 27 PROPERTIES OF END-CAPPED BiCo (1:3) GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE °C (°F)	FLEXURAL PROPERTIES				INTERLAMINAR SHEAR STRENGTH	
	TIME (HRS.)	TEMPERATURE °C (°F)		STRENGTH		MODULUS			
				10 <sup>8</sup> N/m <sup>2</sup>	(10 <sup>3</sup> psi)	10 <sup>10</sup> N/m <sup>2</sup>	(10 <sup>6</sup> psi)	10 <sup>6</sup> N/m <sup>2</sup>	(psi)
38 a *	.1	204 (400)	204 (400)	6.94	(100.6)	11.6	(16.8)	27.8	(4030)
				6.00	( 87.0)	11.5	(16.7)	26.7	(3870)
				7.46	(108.2)	12.8	(18.5)	26.6	(3850)
				6.80	( 98.6)	12.0	(17.3)	27.0	(3920)
	10			7.59	(110.0)	13.7	(19.8)	26.0	(3770)
				6.69	( 97.0)	12.9	(18.7)	25.2	(3660)
				5.61	( 81.4)	11.1	(16.1)	26.8	(3880)
				6.64	( 96.0)	12.6	(18.2)	26.0	(3770)
	100			7.59	(108.6)	12.0	(17.4)	25.2	(3660)
				7.10	(103.0)	11.9	(17.2)	24.2	(3510)
				6.99	(101.4)	11.7	(16.9)	27.8	(4030)
				7.20	(104.3)	11.8	(17.2)	25.7	(3730)
	300			6.40	( 92.8)	12.0	(17.4)	25.0	(3630)
				5.81	( 84.3)	11.9	(17.3)	25.9	(3750)
				5.42	( 78.6)	11.7	(16.9)	24.1	(3490)
				5.88	( 85.2)	11.9	(17.2)	25.0	(3620)
	600			6.48	( 94.0)	11.8	(17.1)	24.1	(3500)
				7.03	(102.0)	12.2	(17.7)	22.4	(3250)
				6.28	( 91.0)	12.1	(17.6)	24.2	(3510)
				6.60	( 95.7)	12.0	(17.5)	23.6	(3420)
	1000			6.16	( 89.3)	12.0	(17.4)	21.9	(3170)
				4.06	( 58.9)	12.1	(17.6)	21.4	(3100)
				6.24	( 90.5)	12.2	(17.7)	21.2	(3070)
				5.49	( 79.6)	12.1	(17.6)	21.5	(3110)

\* Polymer batch PH-1-257 JS16  
 Laminate cure: 1 hr at each 336°C (636°F) and  
 455°C (850°F) and  $2.07 \times 10^6$  N/m<sup>2</sup> (300 psi)  
 Fiber Volume: 61% by weight



TABLE 28 PROPERTIES OF END CAPPED B1Co (1:3) GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE °C (°F)	FLEXURAL PROPERTIES				INTERLAMINAR SHEAR STRENGTH (psi)	
	TIME (HRS.)	TEMPERATURE °C (°F)		STRENGTH		MODULUS			
				$10^8$ N/m <sup>2</sup>	( $10^3$ psi)	$10^{10}$ N/m <sup>2</sup>	( $10^6$ psi)	$10^6$ N/m <sup>2</sup>	
38a*	.1	316 (600)	316 (600)	3.18	(46.1)	6.3	(9.1)	24.2	(3510)
				3.99	(57.9)	8.9	(12.9)	25.0	(3620)
				2.66	(38.5)	7.5	(10.9)	23.4	(3390)
				3.28	(47.5)	7.6	(11.0)	24.2	(3510)
	10			4.49	(65.1)	10.1	(14.7)	17.6	(2550)
				3.94	(57.1)	8.6	(12.5)	17.8	(2580)
				4.27	(61.9)	9.3	(13.5)	18.6	(2700)
				4.23	(61.4)	9.3	(13.5)	18.0	(2610)
	100			2.63	(38.2)	6.9	(10.0)	13.3	(1930)
				4.27	(61.9)	9.4	(13.6)	16.4	(2380)
				3.41	(49.5)	10.1	(14.6)	17.1	(2480)
				3.44	(49.9)	8.8	(12.7)	15.6	(2260)
	300			3.03	(44.0)	7.0	(10.1)	10.6	(1530)
				3.21	(46.6)	7.2	(10.5)	8.6	(1270)
				3.02	(43.8)	7.3	(10.6)	10.1	(1460)
				3.09	(44.8)	7.2	(10.4)	9.8	(1420)
	600			2.87	(41.6)	7.2	(10.5)	3.7	(530)
				2.67	(38.7)	6.9	(10.0)	7.1	(1030)
				2.54	(36.8)	6.2	( 9.0)	4.9	( 710)
				2.69	(39.0)	6.8	(9.8)	5.2	( 760)
	1000			.97	(14.1)	3.3	( 4.8)	-	-
				1.14	(16.6)	2.1	( 3.1)	-	-
				1.65	(23.9)	5.0	( 7.2)	-	-
				1.26	(18.2)	3.5	( 5.0)	-	-

\* Polymer batch PH-1-257 JS16

Laminate cure: 1 hr at each 336°C (636°F) and  
455°C (850°F) and  $2.07 \times 10^6$  N/m<sup>2</sup> (300 psi)

Fiber Volume: 61% by weight

TABLE 29 PROPERTIES OF TAB/m-BPGB GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE °C (°F)	FLEXURAL PROPERTIES				INTERLAMINAR SHEAR STRENGTH	
	TIME (HRS.)	TEMPERATURE °C (°F)		STRENGTH		MODULUS			
				10 <sup>8</sup> N/m <sup>2</sup>	(10 <sup>3</sup> psi)	10 <sup>10</sup> N/m <sup>2</sup>	(10 <sup>6</sup> psi)	10 <sup>6</sup> N/m <sup>2</sup>	(psi)
39 *	.1	204 (400)	204 (400)	6.90	(100.0)	12.6	(18.2)	34.3	(4980)
				7.84	(113.7)	14.8	(21.5)	32.3	(4690)
				7.94	(115.2)	13.3	(19.3)	28.9	(4190)
				7.56	(109.6)	13.6	(19.7)	31.8	(4620)
	10			6.97	(101.0)	14.5	(21.0)	24.3	(3530)
				6.23	( 90.4)	13.2	(19.1)	29.5	(4280)
				6.65	( 96.4)	13.6	(19.7)	33.9	(4910)
				6.62	( 95.9)	13.7	(19.9)	29.2	(4240)
	100			6.77	(98.1)	13.7	(19.9)	26.3	(3810)
				6.39	( 92.6)	13.4	(19.5)	28.6	(4150)
				6.21	( 90.1)	13.3	(19.3)	28.7	(4160)
				6.46	( 93.6)	13.5	(19.6)	27.9	(4040)
	300			6.44	( 93.4)	13.6	(19.7)	23.1	(3350)
				6.31	( 91.5)	13.2	(19.2)	27.0	(3910)
				6.50	( 94.2)	13.7	(19.9)	29.9	(4340)
				6.42	( 93.0)	13.5	(19.6)	26.7	(3870)
	600			6.06	( 87.8)	13.2	(19.1)	29.2	(4230)
				7.72	(112.0)	15.4	(22.3)	28.3	(4110)
				7.61	(110.4)	14.2	(20.6)	24.4	(3540)
				7.13	(103.4)	14.3	(20.7)	27.3	(3960)
↓	1000	↓	↓	7.30	(105.8)	13.6	(19.7)	23.1	(3350)
				6.35	( 92.1)	13.7	(19.8)	21.5	(3120)
				6.81	( 98.8)	13.4	(19.4)	21.4	(3100)
				6.82	( 98.9)	13.5	(19.6)	22.0	(3190)

\* Polymer batch PR-1-247 JS13  
 Laminate cure: 1 hr at each 336°C (636°F) and  
 455°C (850°F) and  $2.07 \times 10^6$  N/m<sup>2</sup> (300 psi)  
 Fiber Volume: 60% by weight

TABLE 30 PROPERTIES OF TAB/m-BPGB GRAPHITE COMPOSITE

LAMINATE NUMBER	EXPOSURE		TEST TEMPERATURE °C (°F)	FLEXURAL PROPERTIES				INTERLAMINAR SHEAR STRENGTH	
	TIME (HRS.)	TEMPERATURE °C (°F)		STRENGTH $10^8 \text{ N/m}^2$ ( $10^3 \text{ psi}$ )		MODULUS $10^{10} \text{ N/m}^2$ ( $10^6 \text{ psi}$ )			
39*	.1	316 (600)	316 (600)	4.23	(61.4)	9.2	(13.3)	27.8	(4030)
				2.87	(41.6)	6.1	( 8.8)	28.2	(4090)
				4.92	(71.3)	11.0	(16.0)	23.4	(3390)
				4.01	(58.1)	8.8	(12.7)	26.5	(3840)
	10			2.99	(43.4)	6.8	( 9.8)	22.5	(3260)
				2.86	(41.5)	7.3	(10.6)	25.1	(3640)
				3.68	(53.4)	9.5	(13.8)	27.3	(3960)
				3.18	(46.1)	7.9	(11.4)	24.9	(3610)
	100			3.28	(47.6)	8.3	(12.0)	23.5	(3410)
				3.55	(51.5)	8.3	(12.0)	24.7	(3580)
				3.91	(56.7)	9.2	(13.4)	24.7	(3580)
				3.58	(51.9)	8.6	(12.5)	24.3	(3520)
	300			3.39	(49.2)	8.7	(12.6)	21.9	(3180)
				1.23	(17.8)	5.4	( 7.9)	23.9	(3460)
				2.79	(40.4)	7.9	(11.4)	25.3	(3670)
				2.47	(35.8)	7.3	(10.6)	23.7	(3440)
	600			2.17	(31.5)	6.3	( 9.1)	24.9	(3610)
				1.34	(19.4)	4.5	( 6.5)	24.6	(3560)
				2.56	(37.1)	7.2	(10.4)	22.6	(3270)
				2.02	(29.3)	6.0	( 8.7)	24.0	(3480)
↓	1000	↓	↓	2.12	(30.7)	2.3	( 3.4)	-	-
				2.37	(34.4)	7.2	(10.4)	-	-
				2.25	(32.6)	5.3	( 7.7)	-	-
				2.25	(32.6)	4.9	( 7.2)	-	-

\* Polymer batch FH-1-247 JS13  
 Laminate cure: 1 hr at each 336°C(636°F) and  
 455°C(850°F) and  $2.07 \times 10^6 \text{ N/m}^2$  (300 psi)  
 Fiber Volume: 60% weight





Figure 28: Cross Section of Laminate No. 38 (X65)

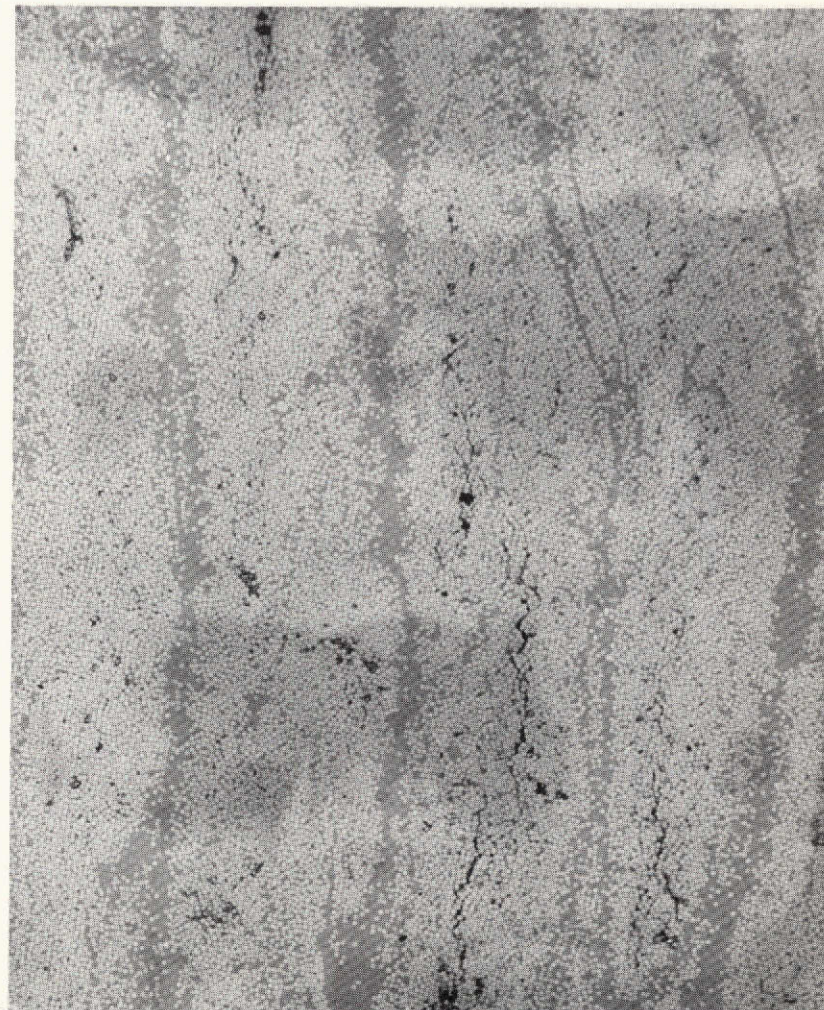
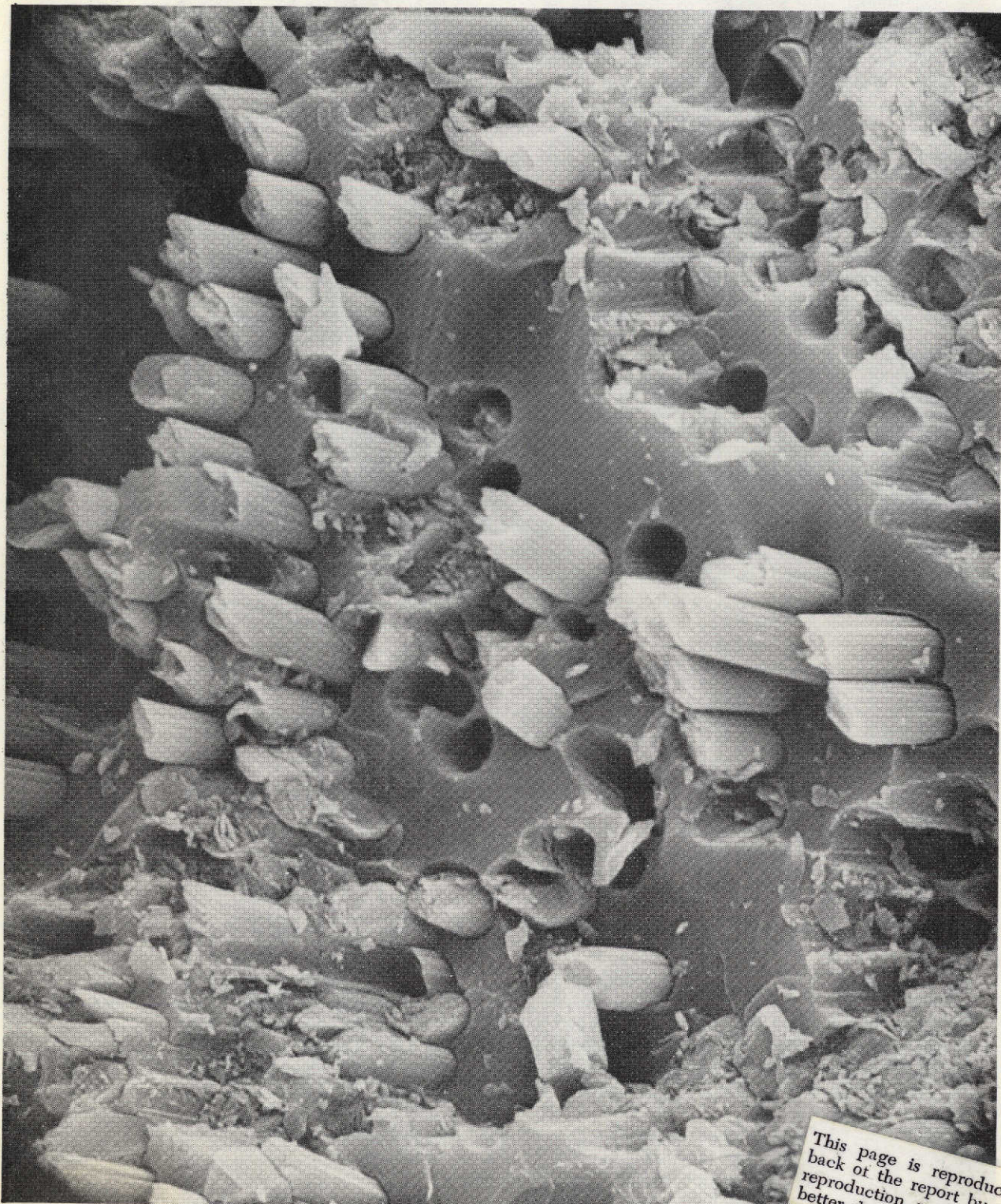


Figure 29: Cross Section of Laminate No. 39 (X65)

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Figure 30: Electron Photomicrograph of Flexural Test Failure Area  
Laminate No. 38 (X600)



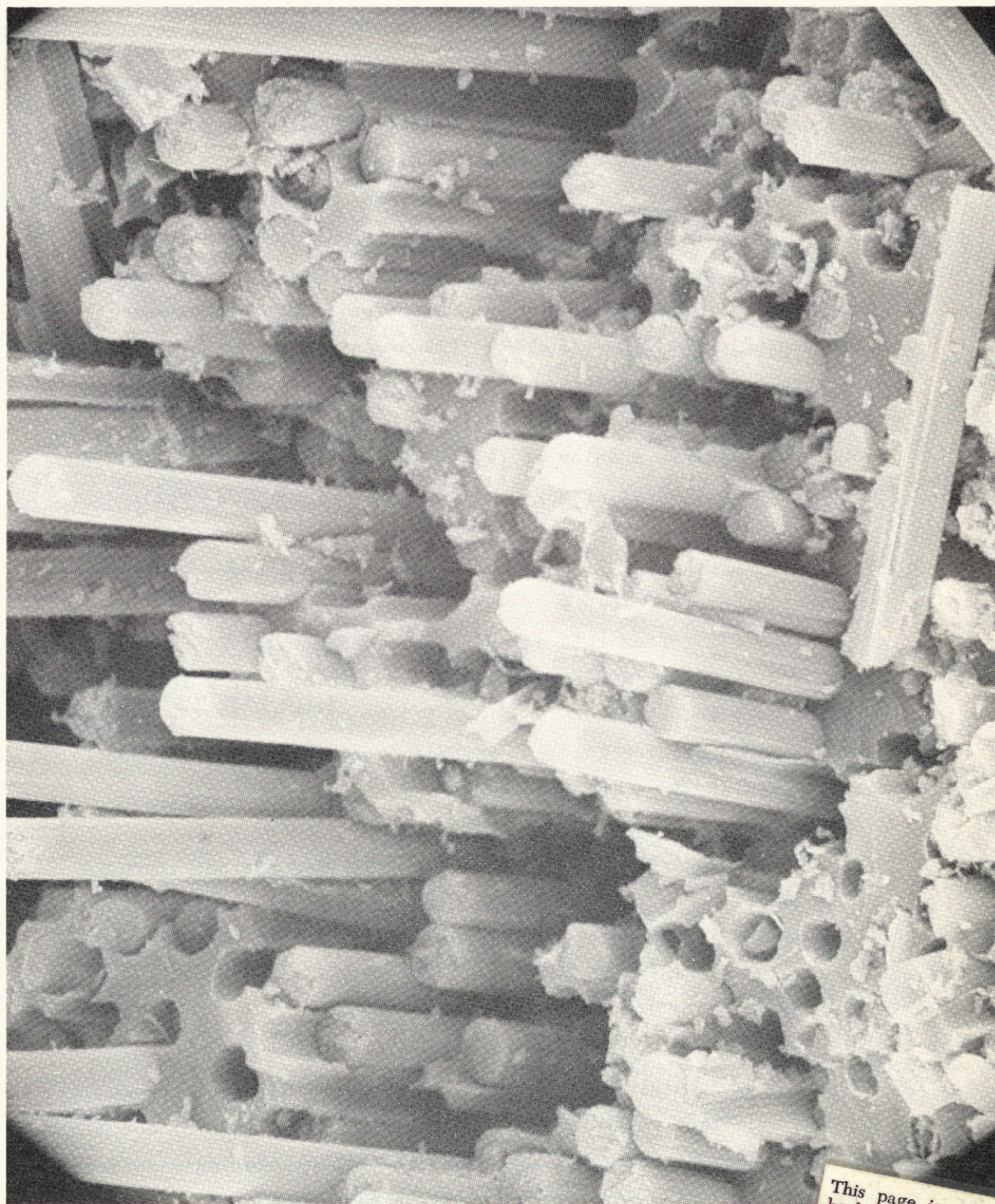


Figure 31: *Electron Photomicrograph of Flexural Test Failure Area*  
*Laminate No. 39 (X600)*

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1. Synthetic modifications of PPQ polymers were shown to be effective in improving processibility, and ambient and elevated temperature mechanical properties of PPQ/HMS graphite composites.
2. Use of the NASA-Lewis developed in situ PMR (Polymerization of Monomeric Reactants) approach for fiber impregnation resulted in improved composite processing and retention of properties after extended aging at 316°C (600°F). PMR process composites derived from a random copolymer exhibited, after 500 hrs exposure in air at 316°C (600°F), a flexure strength of  $3.11 \times 10^8 \text{ N/m}^2$  (45,000 psi) at 316°C (600°F), a flexure modulus of  $14.9 \times 10^{10} \text{ N/m}^2$  ( $21.5 \times 10^6$  psi) and an interlaminar shear strength of  $16.0 \times 10^6 \text{ N/m}^2$  (2320 psi).
3. Modification of BlCo (1:3) by end-capping the polymer yielded composites which were capable of surviving 1000 hours aging in air at 316°C (600°F). After this aging, end-capped BlCo (1:3) composites exhibited at 316°C (600°F) a flexure strength of  $1.26 \times 10^8 \text{ N/m}^2$  (18,200 psi) and a flexure modulus of  $3.5 \times 10^{10} \text{ N/m}^2$  ( $5 \times 10^6$  psi). Without end-capping BlCo (1:3) composites will not survive 1000 hours aging at 316°C (600°F) (Reference 1).
4. PPQ composites derived from TAB/m-BPGB exhibited further improved retention of properties after aging 1000 hrs in air at 316°C (600°F). After aging TAB/m-BPGB composites exhibited at 316°C (600°F) a flexure strength of  $2.25 \times 10^8 \text{ N/m}^2$  (32,600 psi) and a flexure modulus of  $4.9 \times 10^{10} \text{ N/m}^2$  ( $7.2 \times 10^6$  psi).
5. A PPQ polymer containing potential cyano crosslinking groups demonstrated excellent weight retention in air at 316°C (600°F) and 371°C (700°F). The polymer, when treated with p-toluenesulfonic acid and mild heat conditions failed to exhibit a glass transition temperature suggesting crosslinking by cyano group trimerization. The cyano containing polymer could not be incorporated into composites because

5. (Continued)

of its high viscosity. Additional investigations are recommended to improve processibility of cyano containing PPQs since this approach offers a means of reducing polymer thermoplasticity at temperatures below 454°C (850°F). This elevated temperature has been required to reduce thermoplasticity of PPW composites at 600°F.



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Meta-bis(hydroxyphenylglyoxalyl)benzene (m-HPGB) and Meta-bis(p-cyanato-phenylglyoxalyl)benzene (m-CNOGB):- A solution of the diacid chloride of m-phenylenediacetic acid (35.0 g, 0.15 m) and anisole (69 g) in carbon disulfide (150 ml) was added dropwise during 2 hours to a stirred slurry of anhydrous aluminum chloride (49 g, 0.37 m) in carbon disulfide at 8 to 12°C. After complete addition, the dark red reaction mixture was stirred at ambient temperature for 18 hours followed by slowly pouring onto ice and hydrochloric acid. Methylene chloride (200 ml) was used to rinse out the reaction flask and also poured onto the ice. The organic phase was separated, washed twice with cold water, dried over Drierite, and concentrated to dryness. The tan residue was washed twice with n-hexane and dried to yield the intermediate diketone as a tan solid (51 g, 92% yield), mp. 82 - 84°C. Meta-bis(p'-methoxyphenacyl)benzene (51 g, 0.14 m) and selenium dioxide (30.7 g, 0.28 m) were refluxed in glacial acetic acid (1 l.) for 6 hours. The black reaction mixture was filtered hot and the red filtrate treated with charcoal and celite 503 and refiltered. Upon cooling, a yellow solid (40 g, 72% yield), mp. 112 - 114.5°C, separated which was recrystallized from ethanol (800 ml) to afford m-bis(p'-methoxyphenylglyoxalyl) benzene as fluffy yellow crystals (30 g) mp. 116.5 - 117.5°C. Meta-bis(p'-methoxyphenylglyoxalyl)benzene (30 g, 0.75 m) was dissolved in glacial acetic acid (300 ml) and aqueous hydrobromic acid (47-48%, 100 ml) was added. The reaction mixture was refluxed for 22 hours followed by pouring the cooled light red solution into ice water (500 ml). The resulting yellow precipitate was removed, washed with water, and dissolved in aqueous potassium hydroxide solution. After filtration, the red solution was neutralized with dilute hydrochloric acid and the isolated gum washed in boiling water. The resulting yellow solid was isolated and recrystallized from a 4:1 mixture of water and alcohol (900 ml) to afford m-bis(p'-hydroxyphenylglyoxalyl)benzene as a yellow amorphous solid (17 g, overall yield 30.5%). Meta-bis(p'-hydroxyphenylglyoxalyl)benzene (3.74 g, 0.010 m) was dissolved in acetone (100 ml) and

cyanogen bromide (2.7 g, 0.025 m) was added at 5°C. After stirring for a few minutes, a solution of triethylamine (2.5 g, 0.024 m) in acetone (50 ml) was added over a 15 min. period at <5°C. Upon the addition of triethylamine, a yellow precipitate began to appear. The yellow suspension was stirred at 5°C for 1 hour and filtered to yield a yellow solid (3.8 g, 90% yield). Recrystallization of the yellow solid from acetonitrile (350 ml) afforded m-bis(p'-cyanatophenylglyoxalyl)benzene as an amorphous yellow solid (2.3 g, 60% recovery) (mp. 198 - 200°C). The infrared spectrum was consistent with the proposed structure of m-bis(p'-cyanatophenylglyoxalyl)benzene (V, -OCN at 4.35 - 4.5 $\mu$ ). A sample submitted for elemental analysis provided the following results: Calculated for  $C_{24}H_{12}N_2O_6$ : %C, 67.92; %H, 2.86; %N, 6.60. Found: %C, 68.07; %H, 2.98, %N, 6.46.

Para-phenoxybenzonitrile: Para-phenoxybenzonitrile was synthesized from reaction of p-bromobenzonitrile with potassium phenolate. Parabromobenzonitrile was synthesized by refluxing p-bromobenzoic acid (300 g, 1.49 m) for ~2 hours in thionylchloride containing a few drops of DMF. The yellow solution was concentrated to dryness in vacuo to yield a white crystalline solid which was dissolved in toluene and added slowly to dilute aqueous cold ammonium hydroxide solution. The resulting white precipitate was isolated, washed with water, and dried to yield p-bromobenzamide (290 g, 98% yield), mp. 187 - 190°C. Para-bromobenzamide (290 g, 1.45 m) was dehydrated refluxing for 18 hours in toluene (1.5 l) and thionyl chloride (500 ml) followed by hot filtration. The filtrate was poured into ice water, stirred 0.5 hour, separated, and the organic phase washed twice with cold water. Concentration of the organic phase and addition of n-hexane provided p-bromobenzonitrile as a tan solid. Overall crude yield from the acid to the nitrile (238 g, mp. 110 - 113°C; lit. mp. 113°C, Reference 11) was 88%. The preparation of p-phenoxybenzonitrile was accomplished in the following manner. Phenol (58g, 0.6m) and potassium hydroxide (34 g, 0.6 m) were stirred and heated under nitrogen to 210°C during 3 hours to yield potassium phenolate as a white solid. Para-bromobenzonitrile (82 g, 0.45 m) and freshly prepared copper catalyst



were added at  $-190^{\circ}\text{C}$  and stirred for 1 hour at  $190^{\circ} - 200^{\circ}\text{C}$ . After workup, the resulting yellow-orange gum (70 g, 80% crude yield) was combined with another crude crop of p-phenoxybenzonitrile and distilled. The fraction collected at  $136 - 140^{\circ}\text{C}$  under 2 mm Hg (lit. b.p.  $170-174/4\text{mm}$ , Reference 6) solidified to yellow crystals of p-phenoxybenzonitrile, mp  $41 - 43^{\circ}\text{C}$  (lit. mp.  $46^{\circ}\text{C}$ , Reference 7). From 180 g of crude p-phenoxybenzonitrile, distillation provided only 67 g of pure nitrile. Para-phenoxybenzonitrile was also prepared from p-phenoxyaniline by diazotization and reaction of the diazonium salt with cuprous cyanide. The crude p-phenoxybenzonitrile prepared by this route was combined with that prepared above and distilled.

An earlier attempt to prepare p-phenoxybenzonitrile yielded p-bromobenzamide and p-bromobenzonitrile. This was believed to be due to incomplete removal of water during preparation of potassium phenolate from phenol and potassium hydroxide.

Para-bis(p'-cyanophenoxyphenylglyoxalyl)benzene, (p-CPGB): The diacid chloride of p-phenylenediacetic acid (16.1 g, 0.07 m) was reacted with p-phenoxybenzonitrile (29 g, 0.15 m) and anhydrous aluminum chloride (19.95 g, 0.15 m) in sym-tetrachlorethane (150 ml). After pouring onto ice and hydrochloric acid, a tan solid (35.2 g), m.p.  $221-225^{\circ}\text{C}$ , was isolated. The tan solid was recrystallized from chloroform to yield a first crop (14.2g) of the intermediate diketone, m.p.  $223-227^{\circ}\text{C}$ . The diketone (14.2 g, 0.026 m) was oxidized with selenium dioxide (5.77 g, 0.052 m) in glacial acetic acid to the corresponding bis (1,2-dicarbonyl) compound (11.4 g) m.p.  $206-209^{\circ}\text{C}$ . Recrystallization from a mixture of benzene and hexane afforded VII as a yellow crystalline powder (5 g, mp.  $211.5 - 213^{\circ}\text{C}$ ).

Meta-bis(p'-acetylenophenylglyoxalyl)benzene (m-ACPG), (attempted synthesis): The synthesis of m-ACPG was sought through the tetrabromo diketone as precursor. Several attempts were made to synthesize the diketone. Table 31 summarizes these attempts. The following is a representative procedure

TABLE 31

REACTION OF THE DIACID CHLORIDE OF *m*-PHENYLENEDIACETIC ACID  
AND 1,2-DIBROMOETHYLBENZENE

Exp't No. PH-1	R <sub>x</sub> Size, mole	Catalyst <sup>1</sup>	Solvent	R <sub>x</sub> Temp °C <sup>2</sup>	Addition	Results
260-1	0.05	AlCl <sub>3</sub>	CS <sub>2</sub>	5°C	DiBr to diCoCl & AlCl <sub>3</sub>	91% Recovery of diBr cpd.
260-2	0.05	AlCl <sub>3</sub>	CS <sub>2</sub>	5°C	Sol'n of diBr & diCoCl to AlCl <sub>3</sub>	91% Recovery of diBr cpd.
263	0.05	AlCl <sub>3</sub>	Cl <sub>2</sub> HCCHCl <sub>2</sub>	5°C	Sol'n of diBr & diCoCl to AlCl <sub>3</sub>	Obtained 27.5g orange solid, mp 390°C, appears to be polymeric.
268	0.05	SnCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	8°C	Sol'n of diBr & DiCoCl to AlCl <sub>3</sub>	86% Recovery of diBr cpd.

1

Stoichiometric quantity (2 mole catalyst per mole diacid chloride)

2

Initial reaction temperature during addition then ambient temperature

(Experiment No. PH-1-260-1, Table 31) used in the attempted synthesis of diketone VIII. A solution of the dichloride of m-phenylenediacetic acid (11.5 g, 0.05 m) in  $\text{CS}_2$  (150 ml) was added in 45 minutes to a slurry of anhydrous  $\text{AlCl}_3$  (13.3 g, 0.1 m) in  $\text{CS}_2$  (150 ml) at  $< 5^\circ\text{C}$ . To the resulting solution was added dropwise 1,2-dibromoethylbenzene (26.4 g, 0.1 m) in  $\text{CS}_2$  (~200 ml). During addition (1 hour) the solution was held at  $8^\circ$  to  $10^\circ\text{C}$ . After stirring two hours at  $<10^\circ\text{C}$  the solution was dropped into ice/HCl. The resulting system was extracted with methylene chloride. Removal of solvent yielded a solid (24.5 g) which, after crystallization from ether, had a melting point of  $69^\circ$ - $73^\circ\text{C}$ . The melting point 1,2-dibromoethylbenzene is  $73^\circ$ - $74.5^\circ\text{C}$ .

Para-phenoxybenzaldehyde: The preparation of para-phenoxybenzaldehyde was attempted as follows: P-phenoxybenzonitrile (39 g, 0.2 m) was added to a mixture of freshly prepared stannous chloride in absolute ether saturated with hydrogen chloride. A yellow solid formed, presumably the aldimine complex, which was hydrolyzed by an attempted steam distillation. The aqueous distillate was extracted with ether and the ether dried and concentrated to yield a residual yellow oil (9.2 g). The remaining oil in the distillation flask, an orange oil, was extracted with ether, washed well with water, dried, and concentrated to yield an orange oily residue (27 g). The infrared spectra of both fractions were identical, exhibiting C-H stretching vibrations at  $3.5$  and  $3.6\mu$  (from  $-\text{CHO}$ ), strong  $-\text{C}\equiv\text{N}$  absorption at  $4.47\mu$  and strong carbonyl absorption at  $5.95\mu$ . The fractions were combined and distilled through a 3 plate Vigreux column. Although three cuts were taken in the  $130 - 138^\circ$  range at 2mm, each fraction exhibited identical infrared spectra, characteristic of a mixture of the aldehyde and nitrile. Para-phenoxybenzaldehyde boils at  $157 - 160^\circ\text{C}$  under 6mm (Reference 12) and melts at  $55^\circ\text{C}$  (Reference 13). The fractions were combined (30.2g) in ether and extracted with aqueous sodium bisulfite. Acidification of the bisulfite wash followed by extraction with ether provided only a trace of a white solid. The ether solution after extraction with aqueous sodium bisulfite was concentrated to yield an orange oil

whose infrared spectrum again showed the presence of aldehyde and nitrile components.

Meta-Bis(phenylglyoxalyl)benzene (m-BPGB): The following is a representative procedure for synthesis of m-BPGB. Crude meta-phenylenediacetic acid (500g, 2.57 mole) was stirred in thionyl chloride (2.3ℓ) containing a few drops of DMF at ambient temperature for 48 hrs. The dark brown solution was concentrated at temperature <50°C under vacuum to yield a brown low melting solid (602g) which was dissolved in dry benzene (1.2ℓ) and added during 5 hrs. to a slurry of anhydrous aluminum chloride (863g, 6.5 mole) in dry benzene (1.6ℓ) at 8 to 15°C. The resulting dark brown reaction mixture was stirred at ambient temperature for 18 hrs. followed by pouring onto ice and hydrochloric acid. The organic phase was separated and the aqueous phase extracted with methylene chloride. The combined organic phase was washed with water, concentrated to 1.2ℓ, and cooled to yield a tan solid which was washed with petroleum ether. The dried solid (619g) m.p. 85-89°C, was recrystallized from alcohol (4ℓ) to provide a tan amorphous solid (400g) which sintered at 87°C and melted at 89-92°C. Two additional recrystallizations from alcohol provided m-diphenacyl benzene as tan crystals (321g, 27% overall yield), m.p. 90.5-92°C. To a slurry of selenium dioxide (192g, 1.73 mole) in glacial acetic acid (1.4), m-diphenacyl benzene (271g, 0.86 mole) was added and the mixture refluxed for 18 hrs. The black reaction mixture was filtered hot and the filtrate treated with charcoal. Upon cooling, m-bis(phenylglyoxalyl)benzene was obtained as yellow needles (220g, 20% overall yield) m.p. 98-99.5°C (lit<sup>3</sup> mp 98-99.5°C) and by DSC, sharp endotherm, onset at 99°C and peak at 100°C ( $\Delta T = 2^\circ\text{C}/\text{min.}$  in  $\text{N}_2$ ).

Para-bis(phenylglyoxalyl)benzene (p-BPGB). The following is a representative procedure for synthesis of p-BPGB (Reference 10). Para-phenylenediacetic acid (566 g, 2.9 mole) melting at 249° - 253°C (softened at 245°C) was stirred in thionyl chloride (1.7ℓ) at RT for 48 hours to form a turbid orange solution. The orange solution was concentrated to near



dryness at 50°C under vacuum to yield a yellowish orange solid which was washed with n-hexane and dried to yield the diacid chloride as yellow crystals (610g). The diacid chloride (619g, 2.6 mole) was dissolved in dry benzene (1.6ℓ) and added dropwise during 3 hours under nitrogen to a slurry of anhydrous powdered aluminum chloride (842g, 6.3 mole) in dry benzene (~2.0ℓ) at <10°C. After complete addition, the brown reaction mixture was stirred at <10°C for 3 hours, and then overnight at ambient temperature. The resulting dark brown reaction mixture was poured onto ice in hydrochloric acid and stirred 4 hours to yield a gray emulsion. The thick emulsion was transferred to large evaporating dishes and allowed to sit overnight. After decanting the water and drying the residue at 75°C, the resulting solid was pulverized and washed successively with dilute aqueous hydrochloric acid, water, aqueous sodium carbonate, and water. The resulting dry gray solid (872g) was dissolved in DMF (5ℓ), filtered, and cooled to yield light tan crystals which were washed with methanol and dried to afford p-diphenacylbenzene (573g), mp 204-207°C. To a slurry of selenium dioxide (404g, 3.6 mole) in glacial acetic acid (3ℓ), p-diphenacylbenzene (573g) was added and the mixture refluxed for 18 hours. The black mixture was filtered hot, and the yellow filtrate was treated with Celite and charcoal, refiltered, and cooled to provide p-bis(phenylglyoxalyl)benzene (499g) as yellow crystals m.p. 124.5-126°C, [lit. m.p. 125-126°C (Reference 10)].

3,3'-Diaminobenzidine (DAB): This material as received, melted at 174-176.5°C. Recrystallization was accomplished by dissolving 150g portions in deoxygenated water (~6ℓ) containing a pinch of sodium dithionite under nitrogen. The yellowish solution was treated with charcoal, filtered, and cooled to provide light tan needles (105g, 70% recovery) of the tetraamine, m.p. 176-177.5°C, [lit m.p. 179-180°C (Reference 14)].

3,3',4,4'-Tetraaminobenzophenone (TAB): This tetraamine, m.p. 214-217.5°C was recrystallized by dissolving 150g in DMF (1.5ℓ) and adding hot water (~3.0ℓ) to near turbidity. The yellowish solution was treated with charcoal, filtered, and cooled to afford the tetraamine (120g, 80% recovery) as yellow needles, m.p. 216-217.5°C, [lit m.p. 217°C, Reference 15)].

### 8.1.2 Model Compound

Reaction of *o*-phenylenediamine and *m*-bis(*p*'-cyanatophenylglyoxalyl)benzene (*m*-CNOGB) was attempted by mixing equimolar amounts of each compound in chloroform. The mixture was stirred at RT for two hours. Solvent was evaporated by heating the system to ~50°C. After chloroform removal, the orange residue exhibited an infrared spectrum with strong carbonyl absorptions at 5.95 $\mu$  and only weak absorptions at 4.35 to 4.5 $\mu$  characteristics of cyanato groups. The orange residue was dissolved in *N,N*-dimethylacetamine and water added to precipitate a yellow solid which sintered at 270°C, wet at 272°C, and failed to form a complete melt by 290°C, indicative of a mixture of high melting components.

### 8.1.3 Polymers

Homopolymers: The homopolymers reported in Tables 1 and 13 were prepared according to the following general procedure. Para-bis(phenylglyoxalyl)benzene, as a fine powder, was added during ~5 min. to a slurry of the tetraamine in a mixture of *m*-cresol and xylene (1:1) (used 70% of the original volume of solvent). The remaining solvent was used to wash down the residual tetracarbonyl reactant and the reaction temperature (< 35°C) controlled by means of cooling in a water bath. The reaction mixture was stirred at ambient temperature for ~18 hrs. to provide a viscous solution as reported in Tables 1 and 13. A small portion of the solution was slowly poured into methanol in a Waring blender to precipitate a fibrous yellow solid which was then boiled twice in methanol. The yellow polymer was dried at ~130°C in vacuo for 4 hrs. and characterized as shown in Tables 1 and 13.

Hydroxy/3PPQ: Hydroxy/3PPQ was prepared from the reaction of 3,3'-diaminobenzidine (0.01m), *m*-bis(*p*'-hydroxyphenylglyoxalyl)benzene (0.0033m), and *m*-bis(phenylglyoxalyl)benzene (0.0067m) in *m*-cresol. The hydroxy monomer was added first to a slurry of the tetraamine and after ~5 minutes, the other tetracarbonyl monomer added. After stirring

overnight, the polymer was isolated by quenching in methanol and dried. The hydroxy/3 PPQ failed to dissolve in chloroform, symtetrachloroethane, N,N-dimethylacetamide (DMAC), N-methylpyrrolidone, or dimethyl sulfoxide. As a result, the hydroxy groups cannot be successfully converted to cyanato groups. This was surprising since the hydroxy PPQ exhibits good solubility in DMAC.

DAB/p-CPGB: Para-bis(p'-cyanophenoxyphenylglyoxalyl)benzene (p-CPGB) (2.8827g, 0.005m) and 3,3'-diaminobenzidine (DAB) (1.0713g, 0.005m) were reacted in m-cresol (20ml) for 0.5 hrs. to form a very viscous orange solution. Additional m-cresol (10ml) was added and the solution stirred for 1 hour. The viscous orange solution was poured into methanol in a Waring blender to precipitate a yellow solid, which was thoroughly washed in hot methanol and dried at 130°C. The yellow solid failed to redissolve completely in m-cresol, and as a result, no inherent viscosity on this sample was obtained. A second synthesis of the DAB/p-CPGB derived polymer was conducted using a higher solvent content (PH-277-1, Table 1 ). A gel was obtained after 1 hour reaction time. The gel persisted even after addition of sufficient m-cresol to reduce the solid content to ~3%. A film of the diluted system was cast for isothermal aging at 316°C and 371°C.

Block Copolymer: The block copolymer (1:3) was prepared through the following representative procedure: p-bis(phenylglyoxalyl)benzene (12.324g, 0.036 mole) as a fine powder was added during 5 minutes to a slurry of 3,3'-diaminobenzidine (6.333g, 0.0295 mole) in a mixture of m-cresol and xylene (1:1, 50 ml). Additional solvent (25 ml) was used to wash down the residual tetracarbonyl reactant and the mixture stirred at ambient temperature for 4 hours to form a viscous clear orange solution. In another flask, p-bis(phenylglyoxalyl)benzene (28.758g, 0.084 mole) as a fine powder was added to a slurry of 3,3', 4,4'-tetraaminobenzophenone (21.477g, 0.0886 mole) in a mixture of m-cresol and xylene (120 ml). Additional solvent (45 ml) was used to wash

down the residual reactant and the mixture stirred at ambient temperature for ~4 hours, to form a viscous clear orange solution. The solution of the diaminobenzidine oligomer was then added slowly with vigorous stirring to the solution of the benzophenone oligomer at ambient temperature. The viscosity increased, and additional solvent which was used to wash out the benzophenone oligomer's flask was added to reduce the solids content to ~18%. Stirring was continued for 18 hours to provide a stable viscous orange solution of 1:3 block copolymer, which is characterized in Table 1 (polymer No. 2).

End-capped Block Copolymer (1:3): The block copolymer (1:3) was end-capped using the following representative procedure. BlCo (1:3) (10g) was placed into m-cresol (100 ml) and stirred ~16 hours to dissolve the polymer. After adding o-phenylenediamine (10g), the system was stirred over a period of ~16 hours. The resulting polymer was poured into methanol in a Waring blender. The resulting yellow solid was thoroughly washed in hot methanol, dried at 130°C and then dissolved in m-cresol (100 ml) followed by the addition of benzil (10g). After stirring ~16 hours, the end-capped block copolymer (1:3) was isolated, washed with methanol, dried and redissolved in m-cresol to give a solution of 18% polymer content.

Cyanato PPQ (attempted synthesis): In an initial attempt to introduce latent crosslinking sites within the polymer, 3,3'-diaminobenzidine was reacted with m-bis(p'-cyanatophenylglyoxalyl)benzene (compound V) in m-cresol at ~10% solids content. Prior to forming a complete solution, the viscosity increased and then upon complete dissolution of the new tetracarbonyl compound, the solution viscosity decreased. After stirring for 18 hours at ambient temperature, the reddish-orange solution was poured into methanol to precipitate a yellow solid. After thoroughly washing with methanol and drying at 50°C in vacuo, the yellow solid exhibited an infrared spectrum which was not consistent with the proposed



### 8.1.3 (Continued)

structure of the desired polymer (no absorptions characteristic of  $\text{-OCN}$  at 4.35 to 4.5 $\mu$  and a strong absorption at 5.95 $\mu$  characteristic of carbonyl).

### 8.1.4 Impregnation Procedure

The standard method of impregnation consisted of winding one tow of HM-S graphite onto a 30.48 cm (12") diameter drum at 3 tows per cm (8 tows per inch). The diluted polymer solution (18% solids) was poured and distributed on the fiber. When the desired quantity of resin had saturated the fibers, heat lamps were directed on the drum to drive off the solvent. With the drum continuously rotating ( $\sim$ 8 rpm) the prepreg was maintained at 93°C (200°F) until the prepreg was tacky. Subsequently the prepreg was cut from the drum and hung in an oven for 17 hours at 121°C (250°F), and for 7 hours at 177°C (350°F) for additional drying. The prepreg was cut to size for laminating when dry.

## 8.2 Test Methods

### 8.2.1 Interlaminar Shear Strength (Short Beam)

Interlaminar shear (ILS) strength tests were conducted per ASTM Test Method D2344, at a span-to-depth ratio of 4.

### 8.2.2 Flexural Properties

Flexural properties were determined per ASTM Test Method D790 using a specimen 1.27 cm (0.5 inches) wide at span-to-depth ratio of 20.

### 8.2.3 Tensile Properties

Tensile strength and modulus were determined using an IITRI specimen configuration. The tests were conducted per ASTM Test Method 628.

#### 8.2.4            Compression Strength

Compression strength was determined per ASTM Test Method D-695-63T.

#### 8.2.5            IZOD Impact

Notched izod impact tests were conducted per ASTM Test Method 256-56T.

#### 8.2.6            Isothermal Aging

Isothermal aging of laminates was conducted in an air circulating oven preheated to the desired temperatures. Air velocities (non-recirculating) were controlled to a nominal 150 mℓ/min.

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